APPENDIX A4

NEW AGE/LANDMARK

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Quality Assurance/Quality Control Manual
Mobile Laboratory Services
Rev. No. 11

April, 2006

Prepared by:

New Age/Landmark, Inc.
667 West Main Street
Benton Harbor, Michigan 49022
Phone (269) 927-3004
Fax (269) 927-3411

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1.0 INTRODUCTION

1.1 Quality Assurance Manual (QAM) Mission Statement

The goal of New Age/ Landmark Mobile Laboratories is to ensure that business operations are conducted with the highest standards of professionalism in the industry. To achieve this goal, it is necessary that NAL provide not only scientifically sound, well documented, and regulatory compliant data, but also provide the highest quality service experience available in the industry. The goal of the NAL Quality System is to ensure that business operations are conducted with the highest standards of professionalism in the industry. To achieve this goal, it is necessary that NAL provide not only scientifically sound, well documented, and regulatory compliant data, but also provide the highest quality service experience available in the industry, NAL's Quality System is designed to provide a framework for continuous improvement within the organization, minimize systematic error, and to encourage constructive, documented problem solving. NAL's corporate structure is designed to provide a framework for continuous improvement within the organization, minimize systematic error, and to encourage constructive, documented problem solving.

1.2 QA/QC Objectives

The purpose of this QA/QC manual is to ensure accuracy, reliability, and uniformity of each chemist and technician employed by New Age. It is New Age's program objective to establish an internal and external monitoring process, ensuring all test results generated by the field analytical personnel are within the limits of precision and accuracy established for each respective project. This program provides a mechanism of documentation to ensure that all test results are traceable to:

1. The date of analysis.
2. The chemist performing the work.
3. The raw data generated.
4. Procedures, methods, and instruments used for the analysis.
5. Instrument calibrations.
6. Reagent purity.
7. The project-specific QC test samples utilized.

1.3 Levels of QA/QC

Unlike in-house laboratories that utilize an assortment of analytical instruments and employ numerous chemists who are allocated to performing routine analyses on a daily basis, New Age's field analytical units are constantly challenged with a diversity of project scopes. Each client/field project has unique QC criteria that are predicated on specific investigative, budgetary, and regulatory requirements imposed by the client. With this in mind, it is New Age's commitment to

assist its clients in developing project-specific QA/QC objectives necessary to achieve the qualitative/quantitative levels of confidence desired without compromising the imposed work schedule or budgetary limitations (from Superfund sites to Phase I field screening).

1.4 QA/QC Protocol

New Age's QA/QC protocol establishes the daily requirements that are required of each staff member in the field as well as those measures required to ensure the quality of the final analytical report, and that all data generated are properly recorded and archived for future use.

Each chemist is provided with a project-specific QA/QC flow chart that outlines the protocols that must be followed to ensure that the data generated conforms to the project's data quality objectives (DQOs).

Upon completion of each project, a final analytical and QA/QC report will be prepared by the chemist, and subsequently submitted (along with the project DQOs and chromatographs) to New Age's QA/QC officer. It is the responsibility of the QA/QC officer to ensure the accuracy of all analytical results and that all project documentation has been properly archived.

2.0 PERSONNEL AND ORGANIZATION

2.1 Key Personnel

New Age's staff provides clients with customized field analytical services for air, soil, groundwater, leachates, soil gas, and solid waste. To achieve a complete understanding of the New Age staffing structure associated with field analytical services, we have provided an overview of key personnel, their responsibilities, and the minimum level of qualification necessary for each position. The organizational chart can be found as Appendix C.

2.1.1. **President/Laboratory Director** - The President has financial responsibility for all business activities of New Age, including the operational activities of each mobile laboratory. He is additionally responsible for the following:

- Profitability and staffing, budget preparation and monitoring, including revenue growth, expense planning, and capital acquisitions.
- Establishing goals and objectives that complement New Age's corporate goals and monitoring progress toward their completion.
- QA program implementation, enforcement, and ultimate responsibility for decisions regarding QA policies and procedures.

- Ensures all resources of the laboratory are available on an as-required basis.
- Approval of QA/QC manual and project DQOs.
- Coordinates laboratory management, project supervision, and client liaison.
- Oversees project scheduling, employee training, and laboratory safety.
- Assists in daily operations including method development, QA/QC verification, maintenance, and repair of instrumentation.
- Assists QA/QC Officer and Sales Representatives with coordinating laboratory management, project supervision, and business development; overseeing project scheduling, employee training, and laboratory safety; and assisting in method development, QA/QC verification, and maintenance.
- Cost control.
- Adherence to project schedules.
- Manages corporate E-Commerce aspects including web page development.

The President/Laboratory Director must have at a minimum a Bachelor's degree and ten years experience in the environmental analytical field.

In the event that the Laboratory Director will be absent for a period of time exceeding 15 consecutive calendar days, the QA/QC Officer will be appointed to temporarily perform his functions. If this absence exceeds 65 consecutive calendar days, the primary accrediting authority shall be notified in writing.

2.1.2. **Sales Representatives** – The Sales Representatives are responsible for all corporate sales and marketing activities including client management, business development, and proposal preparation. The Sales Representatives are responsible for the following items:

- Development of corporate marketing and sales literature.
- Construction of bid preparation and bid responses.
- Direction of trade show and conference activities.
- Conduction of sales meetings and presentations.

- Responsible for identifying, understanding and documenting client requirements through proposals, work plans, and contracts. Responsible for actively updating the client on the project status and establishing appropriate communications between the laboratory and the client.

- Assessment of new opportunities and discusses availability of staff and equipment with the President. No projects are to be scheduled without prior approval from the President.

- Responsible for assessing concerns and complaints about the company's performance and developing and implementing corrective actions to remedy the situation.

- Responsible for interfacing with appropriate laboratory personnel to communicate project requirements and establish commitments to ensure successful completion of any project.

The Sales Representatives report directly to the President.

2.1.3. **Quality Assurance/Quality Control (QA/QC) Officer** - The QA/QC Officer is responsible for monitoring the quality of the laboratory work and taking appropriate actions to ensure that the standards are being met. The QA/QC Officer reports directly to the President. The QA/QC Officer is responsible for the following items:

- Quality Assurance Program Plan - Preparation and oversight of the laboratory Quality Program.

- Internal Quality Control Measurements - Establishing QC procedures, providing control samples, and setting warning and action limits for every test or parameter to standardize laboratory operation for quality performance.

- Data Review - Regular review of completed projects for QC data quality and compliance with overall quality objectives. Data validations are carried out as requested. Errors, omissions, and deviations from standard protocols may result in short- or long-term corrective action.

- Corrective Actions - Identifying and referring any instances in which the QA/QC objectives are not being met to the Vice President Analytical Services for remedial and corrective action and then following up on that action to assure that QA/QC objectives are once again being met.

- Audits - Reviewing laboratory systems, processes, and documentation for completeness in accordance with the QA Plan.

- Standard Operating Procedures (SOPs) - Aiding in ensuring that the SOPs meet or exceed the requirements of the referenced analytical methods. Verifies that SOPs are available and used by the technical staff. Audits laboratory procedures according to the current SOP.

- Documentation - Developing and maintaining systems for archiving laboratory documentation with review and oversight of laboratory records.

- Subcontracting - Assisting in the selection and audit of subcontractors to ensure compliance with the requirements set forth by New Age.

- Technical quality.

- Trains chemists and technical staff.

- Supervises the calibration, and maintenance of instrumentation.

- Establishes and maintains specific instrument QC limits.

- Establishes analytical methodologies.

- Chairs the senior chemist council (SCC), which validates and approves technical procedure changes.

The QA/QC Officer has the authority to place a Stop Work Order into the laboratory whenever data reliability may be questioned. This Stop Work Order effectively stops analyses until such time as the technical staff can satisfy the concern of the QA/QC Officer that the processes are in control. The Stop Work Order will also prevent any data in question from being reported. The QA/QC Officer must have at a minimum a Bachelor's degree and eight years applied analytical experience, at least 3 of which must have been in the environmental field.

In the case of an extended absence of the QA/QC Officer, these duties will be temporarily assumed by the Laboratory Director.

2.1.4 CHEMISTS & TECHNICIANS

2.1.4.1 <u>Project Chemists</u>

- Analysis - Perform required analyses according to test methods specified by the rule, permit, or QA Plan.

- Calibrations - Ensure that all analytical equipment has been properly calibrated before beginning analytical sequence.

- Documentation - Ensure that all identifying information (including sample ID numbers) have been accurately transcribed into records or computer databases.

- Calculations - Ensure that all calculations are correct.

- Confirmations - Ensure that all confirmatory tests or procedures have been completed.

- Corrective Actions - Identify, document, and begin corrective actions on any quality control problem that relate to the analytical test.

- Daily Instrument Maintenance - Maintain equipment in proper working condition and document all preventative maintenance repairs.

All Chemists report directly to the Senior Chemists. Chemists must have at a minimum a Bachelor's degree or three years applied analytical experience. In addition, they must successfully complete in-house training programs as demonstrated by submission of an Initial Demonstration of Capability (IDOC) study.

2.1.4.3.Senior Chemists

- Specifications - Ensure that all activities are performed according to the methods and protocols approved by the SCC and specified in the QA Plan.

- Data Review - Review all analytical data generated by their respective project staff. This review includes: Checking documentation for completeness and proper sample identification; checking raw data for calculation, interpretation or clerical errors; and determine whether acceptable quality control data is produced.

- Time Management - Coordinate the analytical work to assure that completion of all tasks occur within the required time frames.

- Instrument Maintenance - Oversee instrument preventive maintenance and repair activities.

- Analytical Methods - Evaluate and implement changes to the analytical and QC measures through the SCC.

- Quality Control - Identify QC problems and take measures to correct or eliminate the problem source.

All Senior Chemists report directly to the QA/QC Officer. Senior Chemists must have at a minimum either a Bachelor's degree and five years applied analytical experience, or eight years applied analytical experience. In addition, they must successfully complete in-house training programs as demonstrated by submission of an Initial Demonstration of Capability (IDOC) study.

2.1.4.3. Technicians

- Sample preparation: extraction/digestion and determination of percent solids.

- Assist Chemists and Senior Chemists as required.

- Maintenance of laboratory and glassware.

Technicians must have at a minimum either a high school diploma or GED. In addition, they must successfully complete in-house training programs as demonstrated by submission of a "work cell" style Initial Demonstration of Capability (IDOC) study.

2.1.5. Office Administrator

- Project Reporting - Responsible for orchestrating all participants of the analytical and report production sections of the laboratory to satisfy both the needs of the client and the laboratory. Responsible for direct involvement in the production of the final analytical reports. This may involve either manual or automatic assembly and would include both a detailed review of the report format and a semi-technical review of the analytical results.

- Subcontracting - Responsible for arranging for the appropriate subcontractor services when necessary. This includes arranging for the sample and report shipping commitments, tracking of the work status, and for any and all pricing agreements.

- Responsible for deliverables package to client in requested format.

- Assists with accounts payable and receivable activities.

The Office Administrator reports directly to the President.

2.2 Staff Training Program -Upon hire at New Age/Landmark each employee undergoes formal training to ensure that all job specific responsibilities are addressed. The QA/QC Officer keeps a comprehensive training file for each employee. Upon completion of each training component, the training file is signed and dated by the employee and the trainer.

2.2.1 Technical Training -Before performing an analytical procedure, each chemist and/or technician receives formal training or on-the-project training by the QA/QC Officer, the President, or his or her designee. Training will include, but not be limited to, the following:

1. Briefing on potential dangers and dangerous materials within the laboratory and/or associated with the analysis. Instruction on the correct procedures to minimize these dangers and maintain a safe working environment (see procedures outlined in the Chemical Hygiene Plan and Hazardous Communication Program).

2. The use of the QA/QC manual and project-specific DQOs.

3. Instruction on proper equipment operation.

4. Instruction regarding sample handling and preservation methods.

5. Data reduction and evaluation procedures.

6. The most current Standard Operating procedures.

7. Training to ensure data integrity and quality of work standards.

Approval to perform a particular procedure is granted when the supervisor agrees that the employee has read, understands and has adequate working knowledge of the most current procedure, QC measures, and safety hazards. Technical employees need to demonstrate the ability to successfully analyze a series of four known reference standard or spikes within the specified tolerances (an Initial Demonstration of Capability or IDOC as required by NELAC standards). Annually, each employee will need a repeat demonstration of capability, and QC and Integrity refresher training. Also, refresher training is needed for all affected employees with each SOP revision.

Chemists may be assisted in increasing their technical abilities through specialized seminars and off-site courses.

2.3 Facilities and Equipment

Corporate Office:
667 West Main Street
Benton Harbor, Michigan 49022 Footage: 4,500 square feet

Mobile Analytical Units:

2 - 208 square foot, dual axle, customized analytical trailer
2 - 120 square foot, dual axle, customized analytical trailer
1 - 105 square foot, dual axle, customized analytical trailer
1 - 60 square foot, single axle, customized analytical trailer
1 - 120 square foot customized laboratory truck
1 - 105 square foot customized extraction truck

Analytical Equipment:

2 - HP model 5890/5972 GC/MSD
3 - HP model 5890/5970 GC/MSD
4 – Tekmar model 2000/2016 Purge and Trap Units
1 - HP model 5890 GC/FID/ECD
1 - HP model 5890 GC/ECD/ECD
1 - HP model 5890 GC/FID/NPD
1 - HP model 5890 GC/FID
1 - SRI model 8610 GC/FID
1 - SRI model 8610 GC/PID/ELCD
1 - SRI model 9300 GC/PID/ELCD/FID
1 - Leeman Laboratories PS1000 ICP Spectrophotometer
1 - Perkin Elmer Model 3110 AA Spectrometer with HGA-60 Graphite Furnace
1 - Milestone DMA-80 Mercury Analyzer
2 – Spectrace 6000 XRF Analyzers
1 – Abbott Laboratories 8-Tray Incubator
Assorted wet chemistry instruments and sample preparation equipment

3.0 ANALYTICAL UNIT OPERATIONS

3.1 Methodologies

New Age currently performs a variety of analytical methods. New Age's chemists and technicians have extensive experience in performing the following methodologies.

- Determination of halogenated volatile and non-halogenated volatile organics by USEPA SW-846 Methods 8015, 8260; and 600 Series Wastewater Methods.
- Determination of gasoline range organics using purge-and-trap 8260 mod.
- Determination of diesel range organics using direct injection 8270 mod. or 8015 mod.

- Determination of polynuclear aromatic hydrocarbons and other base/neutral/acid extractables by US EPA SW-846 Methods 8100 and 8270; and 600 Series Wastewater Methods.

- Determination of polychlorinated biphenyls (PCBs) by US EPA SW-846 Method 8082 and pesticides by US EPA SW-846 Method 8081 or 8270.

- Determination of explosives by US EPA SW-846 Method 8095.

- Determination of single and multiple trace metals by US EPA SW-846 Methods 7000 and 6000 Series.

New Age's mobile laboratories are fully capable of following the appropriate USEPA SW-846 and 600 Series Wastewater Methods for all sample analyses. However, in the event that modifications to the approved methods are necessary and authorized by the client's DQO, the laboratory will provide detailed descriptions and supporting documentation prior to laboratory use. The documentation is prepared by the laboratory as necessary and forwarded to the client upon request.

3.1.1 Method Detection Limit Studies

Method Detection Limit (MDL) studies are carried out each calendar year and more frequently as required, e.g., new method implementation or major changes to instrumentation, etc. The MDL is assayed in a liquid or solid matrix according to 40 CFR, Part 136, Appendix B. The determination is based on seven (7) or more replicates at a calculated spiking level. Several iterations, to determine the correct spiking level, may be necessary. A low level standard at the calculated PQL concentration is then assayed to confirm capability.

$$\text{Method Detection Limit} = S^2(t)$$

$$S^2 = \frac{1}{n-1}\left[\sum X^2 - \left(\sum X\right)^2/n\right]$$

t = 3.143 for seven replicate measurements

Where:

$\sum$	=	Sum of the X values from I = 1 to n
X	=	Analytical results in the final method reporting units for seven aliquots
n	=	Number of measurements
t	=	The student t value at a 99% confidence interval for n -1 degrees of freedom
S^2	=	Variance, where S is the standard deviation for n -1

3.2 Equipment and Supplies

3.2.1 Glassware - Accurate and reproducible results begin with clean glassware. Each chemist and technician is trained in "good laboratory practices" to eliminate error or contamination.

Chemists and technicians use glassware and "Hamilton" gas tight syringes that are dedicated to the specific analytes of interest for the performance of environmental analyses. A copy of the Hamilton "Accuracy and Precision Statement of Conformance" is maintained in the office.

Standard solutions and spike matrices are prepared and placed in disposable vials that are secured with Teflon-lined septa caps.

3.2.2 Reagents and Standards - Chemists and technicians will verify expiration dates on reagents received. In the event that a reagent is assigned an expiration date by the vendor that is less than 12 months from the date of receipt, the vendor expiration date will apply. All raw chemical containers are labeled with an expiration date 5 years from the opening date, or the vender indicated expiration date, which ever occurs first.

1. All organic analytical procedures involve the use of certified quality chemicals. Incoming reagents and standards will be labeled with the date received and the date opened. All reagents, standards, and testing materials received will include certificates of analysis that state their purity and accuracy.

2. Reagent blanks will be run for each batch of samples to confirm their ongoing purity and possible contamination subsequent to purchase.

3. Once prepared, organic working calibration standards or spike mixtures will be refrigerated as appropriate. Each calibration standard or spike mixture will be labeled with the standard identification, the initials of the person who prepped the standard, the standard concentration, the book and page number of the standard prep, the standard ID number, the prep date, and the expiration date of the standard.

3.2.2.1 Sources of Approved Reagents and Standards

Instrument Group	Standard Source	How Received	Preparation from Source	Lab Stock Storage	Preparation Frequency
Volatiles	Accustandard or Ultra Scientific	~2000 ppm solution	Intermediate from source	Freezer	Biannually
	Ultra Scientific	~100 ppm solution	Intermediate from source		Biannually
	Chem Serv Accustandard Sigma-Aldrich	Neat	Primary from neat		Annually
			Intermediate from primary		Biannually
			Working from intermediate		Daily
Semivolatiles	Supelco Accustandard	~2000 ppm solution	Intermediate from source	Freezer	Biannually
			Working from intermediate		Weekly
	ChemServ/ Aldrich	Neat	Primary from source		Annually
			Working from primary		Weekly
Inorganics	CPI VWR High Purity	-100 ppm solution -1000 ppm solution	Primary from neat	Laboratory	Annually
			Intermediate from primary		Biannually
	Orion HACH	Variable	Working from intermediate		Biannually
			Working from primary		Biannually

3.2.2.2 Purchasing, Receiving, and Storage of Consumables – All purchases must originate with purchase order authorized by either the QA/QC Officer or the President submitted to the Office Administrator. All reagents and standards will be logged into the Chemical Receiving Log upon receipt, before being taken to the appropriate area for storage. Acids are stored in the Acid Storage Cabinet. Solvents are stored in the Solvent Storage Cabinets; with Purge and Trap grade Methanol having its own cabinet. All other reagents are stored on shelves above the Solvent Storage Cabinets. Volatile and semivolatile standards each have their own freezer for storage. Inorganic standards are stored in cabinets in the metals laboratory.

3.3 Sample Custody

An important link in the sequence of analysis is the documentation necessary to prove that the sample results reported were derived from the sample which was collected. Therefore, samples are physical evidence and are handled at New Age according to established procedures, according to the USEPA, Office of Enforcement, National Enforcement Investigations Center (NEIC), for purposes of legal proceedings. A sample is considered to be in an individual's custody if the sample is: 1) in the individual's physical possession, 2) in the individual's view after being in his/her possession, or 3) the sample is placed in a secure locked limited access location after being in the individual's possession. After sample receipt, the samples are placed in appropriate refrigerators within the secure laboratory area where only authorized laboratory personnel have access.

3.3.1 Field Sample Documentation - when the laboratory receives samples, it is expected that the individual sample containers will each have a sample label attached to them and the samples are accompanied by a chain of custody (COC) record. The sample labels must be attached at the time of sample collection. Any contaminated or damaged samples will be returned immediately to the client. The labels should be written in indelible ink and should contain the following information:

- Site name or project number
- Sample number of field identification
- Date and time of sample collection
- Designation as a grab or composite sample
- Type of sample matrix
- Analyses to be performed

3.3.2 Chain-of-Custody (COC) - Sample analysis begins with the receipt of samples. Once the sample has been collected and properly labeled, the COC record is used to document the integrity of all samples. The COC record is used to record the custody of samples during sample collection, person-to-person transfers, sample shipment, and laboratory receipt. The following information must be present on the COC record:

- Site name
- Site location
- Contact person and telephone number
- Project number
- Sample numbers or field identifications
- Date and time of sample collection
- Designation as grab or composite sample
- Brief description of sample and sampling location
- Number of containers
- Preservative used (if any)
- Types of analyses required
- Name of sampler and signature

- Signatures of people in possession of the sample and when samples are transferred

For cross-reference, all data recorded on the COC must match that of the sample label. As each individual sample is logged, it will be assigned a priority of analysis as specified by the client.

3.3.3 **Sample Storage** - All samples are to be stored in an appropriate manner relative to the analyses to be performed, i.e., refrigerated, etc. All soil and groundwater samples must be received in certified clean sample containers. The chemist will remove the sample from the refrigeration unit only during the sample preparation phase. Upon completion of the sample preparation, the sample will once again be placed back into the storage area. All samples received will be kept in the refrigeration unit while on the client's project site in order to facilitate preservation should duplicate analyses or dilutions be necessary, up to the allowable holding time for its respective analysis. Samples will be carefully stored and monitored to prevent deterioration, contamination or damage.

3.3.4 **Sample Acceptance Policy** - The client or the client's representative carry out all sampling procedures. Prior to the acceptance of any samples, the laboratory sample acceptance policy is conveyed to the sampler. The sampler ensures that proper procedures have been followed in the collection, preservation, and documentation of samples submitted to the laboratory for analysis.

3.3.5 **Representative Subsampling** -When a particular sample contains a variety of matrices; each matrix will be handled as a separate sample. Each separate matrix is indicated by the laboratory ID number, and a separate letter designation for differentiation.

Parameter	Volume	Container Type[1]	Preservation	Max Hold Time
Water/Wastewater Samples[2]				
Petroleum Hydrocarbons (TPH)	1 liter	1L G	Cool 4°C, H2SO4 to pH < 2	7 days until extraction, 28 days after extraction
Phenols	500mL	1L BR	Cool 4°C, HLC to pH < 2	7 days until extraction, 28 days after extraction
Purgeable Halocarbons and Volatile Organics	40mL	40mL Glass vial, Teflon-lined septum	Cool 4°C, HLC to pH < 2	14 days
Purgeable aromatic hydrocarbons	40mL	40mL Glass vial, Teflon-lined septum	Cool 4°C, 0.008% $Na_2S_2O_3$ HCl to pH < 2	14 days, 7 days if not pH adjusted
Semivolatile Organics and Herbicides	1 liter	1L Amber Glass, Teflon-lined cap	Cool 4°C, 0.008% $Na_2S_2O_3$	7 days until extraction, 28 days

Parameter	Volume	Container Type[1]	Preservation	Max Hold Time
				after extraction
Pesticides	1 liter	1L Amber Glass, Teflon-lined cap	Cool 4°C, pH 5-9	7 days until extraction, 28 days after extraction
Metals	200mL	Plastic	PH < 2	6 months except Hg @ 28 days
TCLP	1 liter	Plastic	Cool 4°C	6 months except Hg @ 28 days
Residuals, Soil and Sediment Samples[3]				
Volatile Organics	50g	G, 40mL vial or 4oz widemouth with Teflon silicone septum	Note 4	14 days
Semivolatile Organics	100g	G, 8oz widemouth with Teflon lined cap	Note 4	14 days until extraction, 40 days after extraction
Metals	50g	4oz widemouth with Teflon silicone septum	6 months except Hg @ 28 days	6 months except Hg @ 28 days
TCLP	200g	G, 8oz widemouth with Teflon lined cap	6 months except Hg @ 28 days	6 months except Hg @ 28 days

1. Glass (G), Boston Round (BR).
2. Adapted from 40 CFR Chapter I, Revised as of July 1, 1988. According to Federal Register of Thursday, September 3, 1987, preservation for Oil and Grease may also be performed with HCl.
3. Adapted from Tables 3-1 and 4-1 in *Test Methods for Evaluating Solid Waste*, SW-846, EPA, Third Edition, 1986, and First Update in 1987. The term residuals includes: (i) concentrated waste samples and (ii) sludges of domestic or industrial origin.
4. Soils, sediments and sludges shall be kept cool at 4°C from collection time until analysis. No preservation is required for concentrated waste samples.

* Follow appropriate preservations listed per the aqueous methods for the generated leachate.

3.3.5 **<u>Waste Disposal Plan</u>** - All samples received and analyzed on-site will be returned to the client's representative for proper disposal. New Age staff is not authorized to take permanent possession or dispose of any samples. **Unless authorized by the client and the President, samples are not to be removed from the project site.** All digestates are to be returned to the fixed lab for neutralization, dilution, and subsequent disposal. All extracts are to be brought back to the fixed lab to be disposed of in the appropriate solvent waste barrel in the waste area if the outer garage. PCB extracts containing sulfuric acid have their own barrel. The laboratory has a service contract with Safety Kleen for pick-up and disposal of waste barrels.

3.4 **<u>Review of New Work</u>** – Review of all new work begins with the QA/QC Officer, and proceeds as follows:

- Initial assessment of materials, equipment, and personnel required to perform new work.
- Determination of resources on hand.
- Approval/ Denial by President for capital expenditures for needed assets or staffing.
- Following approval by President, a purchase order is submitted to the Office Administrator and/or new staff is hired if needed.
- Following denial by President, the new work is declined.

4.0 DATA HANDLING

4.1 Data Handling

To ensure the integrity of all data generated by New Age, all laboratory departments adhere to good laboratory practices when reducing, validating and reporting data. Reduction of data starts the flow of information through the reporting system. All data must be validated by meeting all of the specific method requirements and QC check criteria before it can be processed into the final reporting stages.

4.1.1 Data Reduction - Data reduction includes the identification and calculations necessary to convert the raw, instrumentally generated, or chemist observed readings to the reported compounds and their respective concentrations.

4.1.1.1 Data Calculations – Applying any mathematical adjustments, i.e., dry weight, dilutions, or concentrations.

Gas Chromatograph Analysis - The identification of an analyte is based on the comparison of the retention time between the unknown peak and the retention time of a known standard. The concentration is determined using a calibration factor. The equation used for the determination of the calibration factor is performed automatically using a computer algorithm. For each individual calibration standard, a unique calibration factor is calculated as follows:

$$CF = \left(\frac{As}{Cs} \right)$$

Where:

CF	=	Calibration factor (area/nanogram)
As	=	Peak area of standard
Cs	=	Amount of standard (nanograms) injected

For each compound detected in a sample the final concentration calculation incorporates the calibration factor. The final concentration is calculated as follows:

GC Extractable

$$ug/L(ug/kg) = \left(\frac{As \times Vf}{CF \times Vi \times P}\right) \times D$$

Where:

CF	=	Calibration factor (area/nanograms)
As	=	Peak area of target parameter
Vf	=	Final extract volume
D	=	Dilution factor
Vi	=	Sample weight or initial extract volume
P	=	Percent solids in decimal format (if results in dry weight are needed)

Gas Chromatograph/Mass Spectrometry Analysis - The requirements for qualitative verification by comparison of the mass spectra are as follows:

1. All ions present in the standard mass spectra at a relative intensity greater than 10.0 percent (most abundant ion in the spectrum equals 100.0 percent) must be present in the sample spectrum.

2. The relative intensities of ions specified above must agree within ±20.0 percent between the standard and sample spectra. (Example: For an ion with an abundance of 50.0 percent in the standard spectra, the corresponding sample abundance must be between 30.0 and 70.0 percent.)
3. Ions greater than 10.0 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the chemist making the comparison. The verification process should favor false positives.

If a compound cannot be verified by all of the criteria listed above, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the analyte will be reported as present.

In order to list structural isomers as separate analytes, they must have acceptable resolution. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25 percent of the sum of the two peaks. Otherwise, structural isomers should be identified as unresolved peaks. Internal standard calibration procedures are used to calculate the final

concentration values for all gas chromatograph/mass spectrometer methods. The internal standards procedure is based on the addition of a reference compound at a known concentration to the sample being analyzed to establish a response relationship between the internal standard and the analyte being measured. For each individual calibration standard, the internal standard is incorporated while calculating a unique response factor. The equation used for the determination of the response factor is performed automatically using a computer algorithm. For each individual calibration standard the response factor is calculated using the following equation:

Where:

$$RF = \frac{As \times Cis}{Ais \times Cs}$$

RF	=	Response factor
As	=	Characteristic ion peak area for standard
Ais	=	Characteristic ion peak area for internal standard
Cs	=	Concentration of standard injected
Cis	=	Concentration of internal standard injected

For each compound detected in a sample, the final concentration calculation incorporates the response factor. The final concentration is calculated as follows:

GC/MS Extractable

$$ug/L(ug/kg) = \left(\frac{As \times AMTis \times Vf}{Ais \times RF \times Vi \times P} \right) \times D$$

Where:

As	=	Area response for target parameter
AMTis	=	Amount of internal standard in ng
Vf	=	Final extract volume
D	=	Dilution factor
Ais	=	Area of internal standard
RF	=	Response factor
Vi	=	Sample weight or initial extract volume
P	=	Percent solids in decimal format (if results in dry weight are needed)

GC/MS Volatiles

$$ug/L(ug/kg) = \left(\frac{As \times AMTis}{Ais \times RF \times Vi \times P} \right) \times D$$

Where:

As	=	Area response for targeted parameter
AMTis	=	Amount of internal standard in ng
D	=	Dilution factor if necessary
Ais	=	Area of internal standard
RF	=	Response factor
Vi	=	Volume purged in mL or grams
P	=	Percent solids in decimal format (if results in dry weight are needed)

When permitted by the method, if necessary, the least squares method of linear regression for non-linear relationships is employed. This process is performed automatically using a computer algorithm that calculates a best-fit linear calibration curve from the response data at each individual calibration concentration. Response data (peak area) for a detected compound is automatically compared to the best-fit line to determine the compound concentration.

4.1.1.2 Chemist Review - The chemist is responsible for verifying that the instrumentation was operating properly and that all performance criteria have been met. This includes verifying that all deadlines for calibration checks, blanks, and instrument tuning have occurred. They must also ensure that the operational components of the analysis met the specifications of the method and were maintained throughout the analytical sequence. All acquired data must be reviewed by verifying all sample identifications and data reduction calculations, and that all QA/QC data met the method specifications.

4.1.1.3 Field Reporting – Reduced data are transferred to the reporting format and values are reviewed by the project chemist to ensure all sample preparation variables have been taken into consideration, i.e., initial and final volumes, clean-up process, dilution factor, and spike amounts, as well as analyte information. The chemist also verifies that all information pertaining to the sample has been documented correctly (as per COC). Information pertaining to the sample preparation, instrument parameters, sample instrumental activities, instrumental tuning, initial and continuing calibration standards and standard addition, if necessary. Hard copies of chromatograms and mass spectra, strip charts, quantitation, and QC reports for the sample batch are all part of this documentation.

4.1.2 Final Data Validation - The validation of final data generated by New Age is designed as a third party review to confirm that all analytical data meets the method criteria and that the analysis is consistent with all the clients' project objectives. Our process includes integrity checks of raw data and validity checks to ensure that method specified QC criteria have been met and verified. Verification is performed by the QA/QC officer through monitoring of QC sample results and audits of data collection and QC parameters.

4.1.2.1 Data Integrity - The chemist is responsible for the majority of the integrity checks done on all raw data. Most of these checks are performed during the data review process and must adhere to the minimum requirements for each analytical projects DQOs.

1. Initial calibrations and calibration check standards at the frequencies specified in the project DQO.

2. A minimum of one method blank per analytical batch. An analytical batch consists of 1 to 20 samples and will not exceed 20 samples.

3. One laboratory control sample (blank spike) on a per batch basis.

4. Depending on method criteria, duplicate blank spikes, a matrix spike and a matrix spike duplicate sample, or one sample replicate (not spiked due to matrix/method limitations) is analyzed per sample batch. The blank spike, matrix spike, and matrix spike duplicate contain target analytes and are subject to the same extraction procedures used in preparing the Client sample.

5. Retention time windows are established per the method.

In addition to the above requirements, the GC/MS instruments must also adhere to the following:

1. The decafluorotriphenylphosphine (DFTPP) or bromofluorobenzene (BFB) required tuning criteria must be met.

2. Percent recovery calculated from the surrogates added to every sample analyzed by GC/MS must fall within method specified control limits or the sample must be reanalyzed.

3. Area counts of internal standards must be monitored (-50 to +100 % Difference).

The data manager and QA/QC officers are responsible for ensuring that sample documentation has been reviewed. This documentation includes raw data entries and calculations, sample preparation procedures, and instrument maintenance and run logs and both initial and continuing calibrations.

All the parameters of the method criteria must meet the project DQO. When exceptionally permitted departures from procedures and methods are necessary, the project manager will gain written permission from the client prior to analysis.

4.2 Data Reporting

After completion of either automated or manual data entry, the data are assembled into a report package. This report package is then reviewed by the data manager and QA/QC officer for completeness and to ensure that all method quality control criteria have been met. All analytical problems encountered during sample analysis are addressed at this time to provide explanations to the data users.

4.2.1 Significant Digits - New Age chemists will report all results to the maximum significant digits possible based on the rules for calculation of significant digits (R.H. Logan, 1995). Calculated results that are less than the method detection limit will be reported as non-detectable (ND).

4.2.2 Authenticity - Chemists will initial the lower right-hand corner of each field instrument print out and/or notebook page utilized. Final reports will be accompanied by a signed cover page to confirm that the data have been transcribed accurately and the QA/QC criteria have been reviewed.

4.2.3 Report Format - Refer to examples presented as Appendix B.

4.2.4 Logbooks - Logbooks are used for handwritten entry of analysis data where computerized record keeping is not yet available. A document control numbered cover page including the document name, the date issued and the company name (New Age), is obtained from Quality Assurance, and then bound prior to use in the laboratory. Logbooks are numbered by the relevant department prefix, a four-digit number and an extension that defines the document (LOG).

Examples include:

- Standard and reagent preparation logbooks
- Instrument maintenance logbooks
- Sample preparation logbooks
- Dry weights (soil preparation) logbooks
- Instrument run logbooks
- Analysis type logbooks
- Sample run logbooks

4.2.5 Analytical Records

Analytical hard copy records are maintained in New Age's central files. CD-ROMs, which contain the chromatograms for a particular project, are archived by the QA/QC Officer quarterly. These records are maintained for a minimum of ten years.

In the event that New Age transfers ownership all records will be transferred along with the company. In the event that New Age goes out of business, all clients will be contacted for instructions for the disposition of the records.

4.3 Assessment of Data Precision and Accuracy

4.3.1 Precision - Precision is based upon the results of the relative percent differences as calculated from sample duplicates or matrix spike and matrix spike duplicates. The control limits for precision are based on historical laboratory data. Procedures, which do not require matrix spike addition, are subject to duplicate analysis of one sample per batch of up to 20 samples. These procedures include acidity/alkalinity, ash, calorimetry and residue.

Present practice is to include MS and MSD samples on a per batch basis or a minimum frequency of 5%. Duplicate results are compared and the relative percent difference (RPD) is then determined according to the following formula:

Relative Percent Difference

$$RPD = \frac{D1 - D2}{(D1 + D2)/2} \times 100$$

Where:

D1 = Determination #1
D2 = Determination #2

4.3.2 Accuracy - Data accuracy is a reflection of the efficiency of the analytical procedure. Accuracy is determined by use of spiked samples and standard reference materials or laboratory control samples performed at the minimum rate of one set per analytical batch of up to 20 samples. A control chart may be generated using historical laboratory data where control limits are established to assess data accuracy.

Accuracy samples consist of blank (or method) spikes and matrix spike samples. The blank spike is a laboratory generated inert matrix sample (deionized water or Ottawa sand) that is spiked with the targeted analytes of interest and processed with the analytical batch. When one of the samples in the batch has two additional aliquots prepared and spiked with the targeted analytes, these two aliquots are referred to as the matrix spike and matrix spike duplicate. The percent recoveries for the matrix

spike (not the matrix spike duplicate since it is used for precision only) and blank spikes are calculated and stored for statistical purposes. The calculation for the percent recoveries for the blank spike and matrix spike are listed below:

Blank Spike:

$$\%\,\mathrm{Recovery} = \left(\frac{ObservedValue \times 100}{TrueValue} \right)$$

Matrix Spike:

$$\%\,\mathrm{Recovery} = \left(\frac{SSR - SR}{SA} \right) \times 100$$

Where:

SSR	=	Spiked sample result
SR	=	Sample result
SA	=	Spike added

After a minimum of 20 recovery data points have been obtained, the mean and standard deviation is calculated and the in-house laboratory control limits are set using the following equation:

Upper control limit = p + 2Sp
Lower control limit = p - 2Sp

$$= \sqrt{\left(\frac{(\sum\ )}{-1} \right)}$$

Where:

p	=	average percent recovery
Sp	=	standard deviation

Once the control limits have been established, they are used to determine whether an analysis is out of control (OOC). This is done by comparing the spike sample percent recoveries against the control limits. If the recoveries fall outside the control limits, then the system should be evaluated for corrective action. Control limits are determined for each method and matrix as required.

4.3.3 <u>Completeness Control</u> - Completeness is expressed as the percentage of the amount of valid data obtained to the amount of data expected. For a set of data to be considered complete, it

must include all QC data verifying its accuracy and precision. If samples analyzed do not meet all quality control requirements in terms of accuracy and precision for any specific parameter, the sample preparation and analysis is repeated pending adequate volume.

$$\% \text{ Complete} = \frac{\text{Acceptable Results}}{\text{Total Analyses}} \times 100$$

4.3.4 Statistical Review - New Age uses either control charts to monitor long-term variation in setting control limits or method/client specified limits. For each method, control charts represent a quantitative estimate of uncertainty. Short-term control charts, e.g., 20-50 data points may be generated at any time for statistical review by standard criteria for out-of-control condition.

4.4 Confidentiality

It is New Age's policy that its employees maintain confidence with regard to all business or technical information pertaining to New Age or information acquired by New Age in the course of performing analysis or testing.

New Age staff will not disclose the analytical results or any sample information to any party other than the client or an appointed representative of the company that supplied the sample(s). The only exception to this rule is if the client or company representative authorizes, in writing, that the analytical information may be disclosed. The obligations of confidentiality do not apply to information that 1) is or becomes part of public domain, or 2) is required to be disclosed under law.

4.5 Electronic Data Security

4.5.1 Keyboard Lockout Passwords -All in-lab computers are equipped with keyboard lockout passwords. Analytical workstations are rendered inoperable on boot until the keyboard lockout password has been keyed in. For security purposes, the password is not echoed to the screen during entry.

4.5.2 Password Protected In-House Network File Server -All in-house data is stored on a local Windows 2000 file server. The file server is protected by a multi-level password scheme and comprehensive file lockouts. All users have their own unique username and password combinations and each user is restricted to their own files in order to prevent tampering. The administrator account, which has access to the entire file structure, is protected by a unique, secure, alphanumeric password.

4.5.3 Comprehensive Off-Site Data Backup -All in-house data is backed up once per day to an external, removable hard drive. Five days of backup data is stored on the drive. The hard drive is taken off-site every night.

4.5.4 In-House Protective Firewall -The entire in-house intranet, including the file server, is protected by a comprehensive Freesco-Linux firewall. The firewall is configured to disallow incoming requests from the Internet to shield the internal intranet from malicious attack.

5.0 QUALITY CONTROL

5.1 Analytical QC

5.1.1 General Requirements - The following components of analytical QC are related to the sampling of an analytical batch. The procedures described are intended to be applied to chemists. All QC data and records required by this section will be retained by the QA/QC Officer will be made available upon request. The frequencies of these procedures vary dependent on the project-specific DQO.

5.1.1.1 Calibration Standards - Calibration standards are used to calibrate the analytical instruments. Depending upon method and regulatory agency criteria, a calibration blank and up to five calibration standards are used to prepare an instrument calibration curve. NIST standards are used, when available, for calibration standards or for calibration check standards.

Method	Standard Source	# Stds Init. Calib.	Accept/ Rejection Criteria-Initial Cal.	Frequency	# Stds Cont. Calib.	Accept/Rejection Criteria-Cont. Calibr.	Frequency
8010	Commercial	5	< 20% RSD	Init/failure of Cont. Calib.	1	± 15% Predicted Response	Initial and 10%
8015	Commercial	5	< 20% RSD	Init/failure of Cont. Calib.	1	± 15% Predicted Response	Initial and 10%
8020	Commercial	5	< 20% RSD	Init/failure of Cont. Calib.	1	± 15% Predicted Response	Initial and 10%
8080	Commercial	5	< 20% RSD	Init/failure of Cont. Calib.	1	± 15% Predicted Response	Initial and 10%
8100	Commercial	5	< 20% RSD	Init/failure of Cont. Calib.	1	± 15% Predicted Response	Initial and 10%
8260	Commercial	5	SPCC > 0.1 or 0.3* RF CCC < 30% RSD	Init/failure of Cont. Calib.	1	SPCC > > 0.1 or 0.3* RF CCC < 20%	Once per 12 hours
8270	Commercial	5	SPCC > 0.05 RF CCC < 20% RSD	Init/failure of Cont. Calib.	1	SPCC > 0.05 RF CCC < 30% Difference in Calibration factors	Once per 12 hours
8310	Commercial	5	<20% RSD	Init/failure of Cont. Calib.	1	± 15% Predicted Response	Initial and 10%

6010	Commercial	1-4	Cor. Coef. >.995			± 10% Predicted Response	Every 10
Spectro-photo-meter	Commercial	5	>0.995 Correlation Coefficient	Init/failure of Cont.Calib.	1	± 15% Predicted Response	Initial and 5%
7000	Commercial	3-5	>0.995 Correlation Coefficient	Init/failure of Cont.Calib.	1	± 10/20% Predicted Response	Initial and 15%

(*) SPCC criteria is dependent upon the SPCC being evaluated.

RF = Response Factor
RSD = Relative Standard Deviation
SPCC = System Performance Check Compounds
CCC = Calibration Check Compounds, percent difference (%D) calculated from initial calibration factors.

5.1.1.2 Calibration Check Standards - All analytical systems must be in control prior to analysis of any data on the system. For this purpose, a standard at midrange concentration, which is of a different source than the calibration standards, is used as a continuing calibration verification. If the calibration verification standard fails method criteria, corrective action must be taken to locate and correct the problem. Reanalysis may be done according to method criteria. If the problem cannot be located or corrected, recalibration is required.

The frequency for the analysis of check standards is set at a minimum of 10 percent and must be within laboratory established control limits. If the system is not in control, recalibration must be done before proceeding with any analysis. The GC/MS systems are on a twelve-hour time clock, therefore the check standard frequency is a time-related factor. After the criteria for a hardware tune are met, the check standard must be within method specified laboratory control limits or recalibration must be done.

5.1.1.3 GC/MS Tuning Standards - Analysis on the GC/MS system cannot begin until the criteria for a hardware tune are met. Injection of 50 ng of DFTPP (Decafluorotriphenylphosphine) on the semi-volatile GC/MS and 50 ng (40 ng for CLP) of Bromofluorobenzene (BFB) purged on the volatile GC/MS are done to meet this criteria. These criteria must be demonstrated at the beginning of each twelve-hour analytical sequence. All hardware-tuning requirements must meet criteria prior to analysis and must be demonstrated within each 12 (twelve) hour shift.

5.1.1.4 Internal Standards - Internal standards are used as a quantitation reference during the target compound analysis and tentative identification screening process, to enable the detection of a possible matrix problem and as a source for instrument performance tracking. It is necessary that the internal standard has a similar analytical behavior as the compounds of interest. Internal standards are used with all the GC/MS applications. All method criteria must be met prior to continuing with an analysis.

5.1.1.5 Surrogate Spikes - Volatile Applications - Surrogate spikes are used to monitor both the effectiveness of the method in dealing with each sample matrix and performance of the analytical system. Semi-volatile Applications - Surrogate spikes are used to monitor the extraction, clean-up (when used) and the effectiveness of the method in dealing with each sample matrix and the analytical system. Surrogate compounds are added to each QC sample and every client sample. All surrogate recoveries are compared to pre-established recovery criteria on a method specific basis. These criteria must be achieved. If not, sample analysis ends and the project chemist perform the necessary steps to correct the problem.

5.1.1.6 Reagent Blanks - Chemists will analyze reagent blank samples to check for background interferences or contamination as a direct result of sample preparation, and instrumental analysis. At a minimum, one reagent blank will be prepared at the commencement of the day immediately before and after the analysis of a calibration standard. The chemist will also perform a reagent blank immediately after analysis of highly contaminated samples. The reagent blanks will be performed until all compounds of interest are determined to be below the method detection limits.

5.1.1.7 Duplicate/Spike Samples (Matrix Spike) - A duplicate field sample will be analyzed after twenty samples (or the last sample analyzed in the event less than twenty samples have been analyzed). Analytes stipulated by the analytical method or by other specific requirements are spiked into the sample (at known concentrations). Selection of the sample to be spiked and/or split depends on the information required and the variety of conditions within a typical matrix. The sample selection will be guided by the objective of spiking which is to determine the extent of matrix bias or interference on analyte recovery. Specific spiking procedures can be referenced in the method of analysis manual.

1. Method Blank - A matrix equivalent sample, i.e. water, soil used to check reagent or process introduced contamination during the method preparation. A blank is prepared with each batch of samples and carried through the entire analytical process.

2. Lab Control Spike - A matrix equivalent sample spiked with a known concentration and carried through the entire analytical process with each batch. When insufficient sample is available for matrix spiking, a duplicate method [blank] spike is prepared to provide a measure of precision.

3. Matrix Spike - A representative matrix sample is spiked with a known concentration and carried through the entire analytical process with each batch.

4. Matrix Spike Duplicate - A duplicate representative matrix sample is spiked with a known concentration and carried through the entire method preparation process with each batch.

5.2 Additional Quality Control Checks

5.2.1 Quality Control Check Samples - Quality control check samples are sent through the laboratory as single and double blind samples. A single blind sample permits knowledge of the unknown parameters but not the concentration, whereas a double blind sample reveals nothing about the unknown. The single and/or double blind samples are generated by the QA/QC Officer or the Vice President Analytical Services as a training/performance check, as a follow-up to corrective action, and/or in response to an internal audit deficiency. Check samples are obtained from NIST or CRADA contracted suppliers.

5.2.2 Field Quality Control Checks - Field quality control checks are assayed and reported in the same manner as samples. In no case is a field quality control sample used in place of laboratory quality control checks. When sample kits are sent to a client's remediation site for use in sampling, all field QC sample containers required for use at the site are included.
A trip blank may be received to be assayed for volatile organics. This sample is organic-free water used to monitor accidental or incidental contamination when sampling for volatile organics and is typically included with all incoming samples. A temperature blank, when received, may be used to measure the cooler temperature upon sample receipt.

5.2.3 Replicate Samples - A replicate sample is analyzed simultaneously when required by the method. This application is employed more in the conventional wet chemistry area of the laboratory than any other area. These samples are used to verify the precision of the method application.

5.2.4 Solvent Purity Checks - High purity solvents are purchased from a single vendor and have been for many years with no contamination problems to date. Clean method blanks indicate that reagents utilized for an analytical determination did not contribute to the presence of an analyte. Solvent purity checks would be done on each solvent lot, if a new vendor is chosen, prior to introduction into the analytical system to ensure the absence of possible contaminants. This is accomplished by concentrating down a set volume of solvent to one mL and analyzing by both GC/MS and GC. All data is recorded in a log and retained in our records. The solvents must contain less than the low-level detection limit of any targeted analytes. If there is a rejection of the solvent lot due to contamination, a new lot is requested from the vendor. Reagent lot numbers are recorded in the laboratory logs with each analysis.

5.2.5 Glassware Cleanliness

5.2.5.1 Laboratory Glassware - When possible, disposable glassware is used. Since all of the laboratory glassware is not disposable, rigorous cleaning procedures have been implemented. New Age follows accepted procedures for cleaning laboratory glassware. Cleaning procedures differ based on the intended use of the glassware, but always include washing in phosphate-free detergents, tap-water rinses followed by deionized (DI) water rinses. Glassware may also be acid or solvent rinsed or soaked as appropriate for the intended use.

The first stage in glassware cleaning always begins with the chemist. Laboratory personnel utilizing non-disposable glassware are responsible for the initial stages of glassware cleaning. That person is responsible for disposing of any remaining reagents or residual sample in an appropriate waste stream and rinsing the glassware, with either water or a solvent, before final cleaning. The glassware is then submitted to the glassware cleaning group for further processing within the laboratory as per the company's Standard Operating Procedure for handling glassware.

6.0 INSTRUMENTATION

6.1 Instrument Manuals

Copies of the instrument manuals will accompany the chemist or technician when performing a project for a client in the field. Original copies are maintained within the company.

6.1.1 Instrument Maintenance

GAS CHROMATOGRAPHS	**(including Mass-Spectrometer components)**	
Semi-Volatile Applications	Change septum	Daily
	Change glass wool in insert (capillary systems)	Daily
	Change packed column glass wool	As needed
	Clip front of guard or analytical column (capillary)	Daily
	Replace first inch of packing	As needed
	Replace column	As needed
	Change moisture, oxygen, hydrocarbon traps	Every 6 months
	Clean injection sleeve/seal	As needed
Volatile Applications	Change septum	As needed
	Clip column (capillary)	As needed
	Replace glass wool	As needed
	Replace first inch of packing	As needed
	Replace column	As needed
	Change moisture, oxygen, and hydrocarbon traps	Every 6 months
DETECTOR SYSTEMS (Chromatographic)		

Electron Capture	Bake-out at 340^{o}C	As needed
	Remove and send for cleaning	As needed
	Source leak test	Semi-Annually
Electrolytic Conductivity	Refill electrolyte reservoir	Weekly
	Replace ion exchange resin	As needed
Electrolytic Conductivity	Replace electrolyte solvent	As needed
	Change teflon transfer line	As needed
	Replace nickel reaction tube	As needed
Flame Ionization	Clean collector in place	Weekly or as
	Remove and clean collector	As needed
	Remove and clean flame jet	As needed
Photoionization	Clean lamp window	As needed
Mass Selective	Replace filaments	As needed
	Clean source and quadrupoles	As needed
	Change roughing pump oil and filters	At 6 months
	Change turbo-molecular oil	Annually

6.1.2 <u>Maintenance Records</u> - Records of maintenance performed on each instrument are found on maintenance logs. Maintenance logs accompany each instrument to the field. Routine and non-routine maintenance is recorded on the maintenance log. The chemist is authorized to perform routine maintenance as indicated in New Age's maintenance SOP. Non-routine maintenance is restricted to the senior chemist or an authorized representative of the GC manufacturer.

When maintenance is performed on an instrument, the following information will be recorded in that instruments field instrument notebook: date of repair, a brief description of the maintenance performed, and the initials of the employee performing the maintenance or repair.

The President will periodically review the instrument maintenance logs for completeness. Instrument maintenance problems will be addressed on an as-needed basis.

The President will maintain an adequate inventory of repair parts for all instruments to ensure that repair parts are on hand to eliminate costly time delays. As repair parts are used, replacement parts will be ordered.

It is the responsibility of each chemist (who performs the instrumental analysis) to inform the President of the condition and repair part(s) needed for each instrument.

6.1.3 Unserviceable Instrumentation - All field instrumentation utilized for analysis that is not performing adequately will be labeled with a red tag. This tag will identify the deficiency, include the name of the instrument, serial number, date, and the name of the person applying the tag. This tag will remain on the instrument until repair or calibration occurs and the instrument has been verified operational and accurate by the analytical manager. Chemists will inform the President of unserviceable instrumentation. If deemed necessary, the President will reallocate instrumentation as needed.

6.1.4 Performance and System Audits

6.1.4.1 Performance Testing - On a semi-annual basis, New Age's analytical staff will conduct a performance evaluation. This performance evaluation will consist of participating in third party QC standard analyses (concentrations known only by the vendor). The analytical staff will analyze these samples, perform the necessary QA/QC, and then forward the results to the vendor. New Age's results, as received by the vendor, will be rated as either "acceptable," "marginal," or "unacceptable." For results returned as "unacceptable," a corrective action report will be filed. This corrective action report will include why the result was out of range and what modifications have been made to correct the problem. In addition, the report will include an evaluation or verification that the problem has been resolved.

6.1.4.2 System Audits - A formal audit will be performed on an annual basis by the QA/QC Officer to ensure compliance with the QA/QC system. The audit will include data management, data collection, analytical performance, evaluation of measurement systems, precision, and accuracy. The audit will also review problems that may have been encountered during previous internal audit, performance testing results, or client complaints.

In the event that any deficiencies are encountered, the President will be notified. Any deviation or non-conformance encountered will be duly noted in a written statement. The vice president will then initiate a corrective action plan. If it is determined as a direct result of the system audit that any results were affected by such deficiencies, the client will be immediately notified in writing.

The end result of the corrective action plan is to resolve any noted deficiencies. It also functions as verification/validation that QA/QC audits have actually resolved the problem(s).

The QA/QC Officer will maintain a file of system audits. The QA/QC Officer will compile the results and forward them to President. The QA/QC Officer will use the audit checklist (refer to Section 6.14.2.1) as a guide in the performance of the audit.

6.1.4.2.1 Audit Checklist

1. Proper QC samples are routinely being used.

2. Proper calibration techniques are being followed.

3. Proper blanks are being run.

4. Surrogates are run.

5. Field analytical accommodations, test areas, energy sources, lighting, heating, ventilation, computer software, instrumentation, etc., are sufficient to facilitate proper performance of required tests.

6. Adequate measures are being exercised to ensure good housekeeping in the mobile laboratory.

7. Proper matrix spikes, trip blanks, etc., are being run.

8. Instrumentation is properly maintained.

9. Maintenance is documented.

10. Adequate facilities, including cold storage for samples, reference materials, and standards are available to preserve identity, concentration, purity, and stability.

11. Calibration of instruments is being performed and documented.

12. Glassware is cleaned in the manner as specified in the Analytical Department SOPs.

13. Coolers are used in the field to store analytical samples. Samples and standards are kept under ice while in the field.

14. Methods of analysis, instrument manuals, maintenance logs, COC logs, and field notebooks are readily available and being used by the chemists.

15. Reference materials, reagents, and standards are properly labeled per SOPs.

16. Client reports are properly archived.

17. Corrective action reports are being utilized and properly archived.

18. Any deviations from the test method are documented and reported to the client.

19. Test data is verified and validated per SOPs.

20. Standard calibration curves are being used to adequately correlate the expected concentrations of analytes.

21. Reagent blanks are being run.

22. Test items are properly received, stored, documented, retained, and disposed of per SOPs.

23. Adequate staffing is available to handle sample load.

24. Any presence or detection of either internal or external interference/pressure to alter results.

25. Adequate instrumentation on hand to perform analysis.

26. Adequate level of staff training present to perform analysis.

27. Adequate spare parts are available to repair instrumentation.

28. Adequate time is afforded the chemists to prepare their instrumentation prior to departing with the mobile laboratory to a project site.

29. Mechanism in place to handle technical complaint issues.

30. Mechanism in place to resolve maintenance issues.

6.1.4.3 Corrective Action -The Corrective Action Request (CAR) process used at New Age is designed to affect both field (short) and long term systematic improvements in the daily laboratory operations. Field corrective actions are usually performed by the chemist during sample analysis procedures. These would include items such as clipping columns or cleaning injection ports. These are items under the direct control of the bench level chemist and must be corrected for analyses to be completed. These out-of-control events are recorded in the instrument or maintenance logbooks for weekly review documentation and follow-up by the supervisors. The instrument logbook references the page number of the maintenance log that contains the pertinent corrective action information. Long-term corrective actions are necessary to correct repetitive problems or unusual occurrences or trends. New Age specifies that any performance evaluation samples, which were reported in error, must undergo the long-term (formal) corrective actions. The long-term corrective actions are documented and followed up completely through the QA/QC Officer.

6.1.4.3.1 Field Corrective Actions - The individual chemist is charged with the responsibility of executing corrective actions upon discovery of problems that may affect the quality of results. It is imperative to document these occurrences so that if they reoccur, the method for resolving the situation is available. The chemist will determine if there is a problem as a direct result of unusual

instrument behavior, matrix interferences during the analysis, checks or spikes being out of tolerance, surrogate recoveries being out of tolerance, or anything else that could adversely affect the quality of data produced. The chemist will attempt to correct the problem immediately. If the problem is corrected, the chemist will rerun those samples in question. If the chemist is unable to correct the problem, he or she will contact New Age's corporate office and consult with the President. These two individuals will attempt to assist the chemist to repair or correct the problem. If these two individuals are unable to correct the problem, the instrument manufacturer will be contacted to assist with repair or correction of the problem. If it is determined that repair or correction is not possible, every attempt will be made to procure additional instrumentation. It is New Age's commitment to maintain communication with the client during this period and make a concerted effort to fulfill its contractual obligations.

6.1.4.3.2 Long Term Corrective Actions - As a result of internal or external audits, Quality Action Reports (QARs), repetitive errors, customer complaint or an observed trend, a CAR may be initiated. Additionally, when proficiency evaluation sample results are received, generated in-house as blind quality control checks or as graded studies, the following protocols are observed to initiate and follow up on corrective actions.

6.1.4.3.2.1 Corrective Action Request Initiation - Initiation of a CAR involves defining the issue or concern with any applicable recommendations included. The date and the name of the originator are included to provide hard-copy final resolution of the action to that individual. The QA/QC Officer generally initiates a CAR upon receipt of proficiency evaluation results or audit findings. Corrective action forms may be generated by any laboratory employee to correct any suspected or observed deviation. This type of CAR may also address long-term fix issues that require team effort and/or frequent assessment of quality objectives.

6.1.4.3.2.2 Corrective Action Request Processing and Tracking - After the issue is identified from available data it is recorded on the corrective action request form. The CAR form has as its major components:

- Computer job number (for daily status tracking)
- Assigned department
- Date initiated
- Originator
- Issue requiring corrective action
- Person(s) assigned the task of identifying the source(s) of error and remedial or corrective action
- Action plan
- Date by which corrective action plan will be completed.
- Raw data review checklist: Calculation, calibration, dilution, instrument problems, SOP review/revision

- Investigation results
- Preventive/corrective action
- Training plan
- SOP revision/review
- Location of the data
- Review and approval personnel signatures
- Copy/distribution list

The CAR document is entered on the QA CAR log by the QA/QC Officer and is then given to the President for assignment to responsible laboratory personnel.

6.1.4.3.2.3 Corrective Action Review and Processing - The action plan and findings in each step of the corrective action process, are reviewed at the QA weekly meetings or more frequently, as necessary, with the personnel assigned the CAR. Guidance, recommendations, information, with experimental and historical data, are introduced to identify all components or sources of error relevant to the issue. A plan to prevent a recurrence of the error or deviation is defined, implemented and summarized in the conclusion section of the CAR.

1. Review of Relevant Data: As a first step, all existing data are reviewed for errors in transcription, calculation, deviations from operating procedures/methods, errors in sample preparation, e.g., dilution, omission, and to provide additional experience to the reviewer in future error checking efforts.

2. Detection Limit Evaluation: Detection limits are reviewed to determine whether the analyte is within the range of detection. Calibration curves may be reset at lower levels when possible to permit detection.

3. Standards Validation: Stock, intermediate, and working standards are evaluated to determine accuracy, correct selection of standard for analysis and whether standard expiration requirements have been met.

4. Instrument and Equipment Performance: Analytical instrument performance is evaluated as is equipment used in the analytical process. Repair work or parts replacement is completed for any instrument/equipment components judged inoperable or marginally operable. Necessary recalibration is performed in addition to regularly scheduled calibrations.

5. Re-analysis of Sample: When sufficient sample remains for re-analysis or a sample which approximates the original proficiency sample can be prepared or purchased, additional assays may be run to assign cause. Original analysis conditions are duplicated in an attempt to reproduce the error for an evaluation of cause.

6. Contamination and Matrix Interference Effects: Where matrix effects exist or when contamination is evident upon reanalysis, measures are taken to identify a solution to the contamination problem to prevent recurrence.

7. Training: Where it is determined that the error resulted from a deviation from the established operating procedures/methods, standard analytical protocols or previous training, additional training is provided as a group or individually by the QA/QC Officer or his designee. Training is reviewed in the event of indeterminate error or when assignable cause for the error is uncertain.

8. Operating Procedure Review/Revision: Standard operating procedures (SOPs), forms, instrument logs and other operating documents are reviewed for errors, omissions and applicability to the analytical procedure. Updates and/or revisions may be made to reduce the incidence of analytical error.

6.1.4.3.2.4 Corrective Action Approval - The document receives final review and approval by the President, then is signed by the assignee(s) and the QA/QC Officer. Copies of the completed CAR form, attached data and any relevant information are distributed to interested laboratory personnel and the originator (to complete the "loop" and provide a vehicle to notify project and/or laboratory personnel of the problem and the resultant corrective action). The original remains on file in the QA office.

6.1.4.3.2.5 Corrective Action Follow-up - Corrective actions are tracked in the QA log by category. The QA log will be reviewed weekly by the QA/QA Officer to ensure that corrective actions are discharged within the agreed time frame. When errors are observed to be repetitive, a corrective action addressing the repeated problem may be generated by the QA/QC Officer. Additionally, a blind sample or follow-up review of a process that has undergone corrective action may be done by the QA/QC Officer or President.

6.2 Additions or Changes to the QA/QC Manual

Occasionally, it may be necessary to modify QA/QC protocol. In such cases the following steps must be taken to implement the new protocol:

1. A rough draft must be submitted to the QA/QC Officer.

2. The QA/QC Officer check that the new protocol complies with all requirements and guidelines.

3. The QA/QC Officer will write a formal version of the new protocol.

4. The new version will be signed and dated by the QA/QC Officer.

5. The document must be approved by the President.

6. The document control number will be changed to signify a new revision.

7. The new version will be added to the QA/QC manual.

When a concern is expressed challenging analysis performed by New Age's analytical staff, this information will be forwarded to the QA/QC Officer for documentation and investigation.

The documented information will include the contact name, company name, nature of the concern, analysis number or project number, date, time, and any other pertinent data. A concern will be considered to be any question challenging the validity of a result or the supporting QC.

When a concern implies non-compliance with the quality control system, an audit will be performed by the QA/QC Officer concentrating on the area of concern. If non-compliance is discovered, the President will be notified immediately. The client will be promptly notified if the non-compliance threatens the accuracy of their results. In the event that the internal investigation reveals that non-compliance is the direct result of a chemist's failure to follow protocols, that chemist will face disciplinary actions.

The QA/QC Officer will establish and maintain a technical complaint log. Periodically, the QA/QC Officer will review the log to ascertain if patterns are forming which indicate the need for improvements or an addition in the QA/QC system.

6.3 Annual Management Review of Quality Systems

On the second Monday of each year, laboratory management will conduct an annual review of New Age's quality system and its testing activities, in order to ensure its continuing suitability and effectiveness and to introduce any necessary changes or improvements in the quality system and laboratory operations. Representatives from all management areas of the company will attend. At the meeting the following points will be addressed:

- Reports from managerial and supervisory personnel
- Outcomes from recent internal audits
- Assessments by external bodies
- Results from inter-laboratory comparisons or proficiency tests

- Changes in the volume and type of work undertaken
- Feedback from clients
- Corrective actions taken.

The minutes from this meeting will reflect any findings and actions, and will be kept as a permanent record by the QA/QC Officer.

APPENDIX A

Accuracy - The nearness of a result or the mean of a set of results to the true value. Accuracy is assessed by means of reference samples and percent recoveries.

Analytical Batch - The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples that are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition.

Blank - A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix; however, a universal blank matrix does not exist for solid samples, and therefore, no matrix is used. The blank is taken through the appropriate steps of the process.

Calibration Check Standard - A verification of the ratio of instrument response to analyte amount. A calibration check is done by analyzing a standard solution of known analytes in an appropriate solvent matrix.

Check Sample - A blank that has been spiked with the analyte(s) from an independent source in order to monitor the performance of the analytical method. The level of the spike will be at the regulatory action level when applicable. Otherwise, the spike will be at five (5) times the estimate of the quantification limit. The matrix used will be phase-matched with the samples and well characterized, i.e., reagent grade water is appropriate for an aqueous sample.

Equipment Blanks - Aliquots of reagent grade water poured appropriately over or through the sample collection device, collected in a sample container, and returned to the mobile laboratory as a sample. Equipment blanks ensure sampling device cleanliness. For projects involving soil gas analysis, equipment blanks consist of ambient air drawn through the collection equipment.

Environmental or Field Sample - A representative sample of any material (aqueous, nonaqueous, or multimedia) collected from any source for which determination of composition or contamination levels is requested or required. For the purposes of this manual, environmental samples will be classified as follows:

a. Surface Water and Ground Water.

b. Drinking Water - delivered (treated or untreated) water designated as potable water.

c. Water/Wastewater - raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents.

d. Sludge - municipal sludges and industrial sludges.

e. Waste - aqueous and nonaqueous liquid wastes, chemical solids, contaminated soils, and industrial liquid and solid wastes.

Field Blanks - Aliquots of analyte-free water or solvents brought to the field in sealed containers by either the client or the chemist. The field blank is exposed to the ambient air without exposing the material to sampling conditions. These samples will be used to determine the amount of background contamination that could arise from the sample(s) being collected at the field site. Field blanks are designed to confirm the lack of contamination as a sample goes through the analysis process.

Matrix/Spike Duplicate - In a matrix or spike duplicate, a predetermined quantity of stock solution(s) of certain analytes are added to a sample matrix prior to sample extraction/digestion and analysis. The sample is split into duplicates, spiked, and analyzed. Percent recoveries are calculated for each analyte detected. The relative percent difference between the samples is calculated and used to assess analytical precision. The concentration of the spike should be at the regulatory standard level or the estimated or actual method quantification limit. When the concentration of the analyte in the sample is greater than 0.1%, no spike of the analyte is necessary.

Method Quantification Limit (MQL) - The minimum concentration of a substance that can be measured with a relative degree of confidence and reported.

Minimum Reportable Concentration (MRC) - The minimum reportable concentration of which any value higher than MRC is reported to the client as annotated on the GC summary sheet. Any value less than MRC is annotated as: <MRC.

Precision - The measurement of agreement between a set of replicate results among themselves without assumption of any prior information as to the true results. Precision is assessed by means of duplicate/replicate sample analysis.

Practical Quantification Limit (PQL) - The lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

Reagent Blank - A reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch.

Reagent Grade - Synonymous term for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

Replicate Sample - A sample prepared by dividing it into two or more separate aliquots. Duplicate samples are considered to be two replicates.

Standard Curve - A curve that plots concentrations of known analyte standard versus the instrument response to the analyte.

Surrogate - Organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples, and field samples prior to analysis. Percent recoveries are calculated for each analyte.

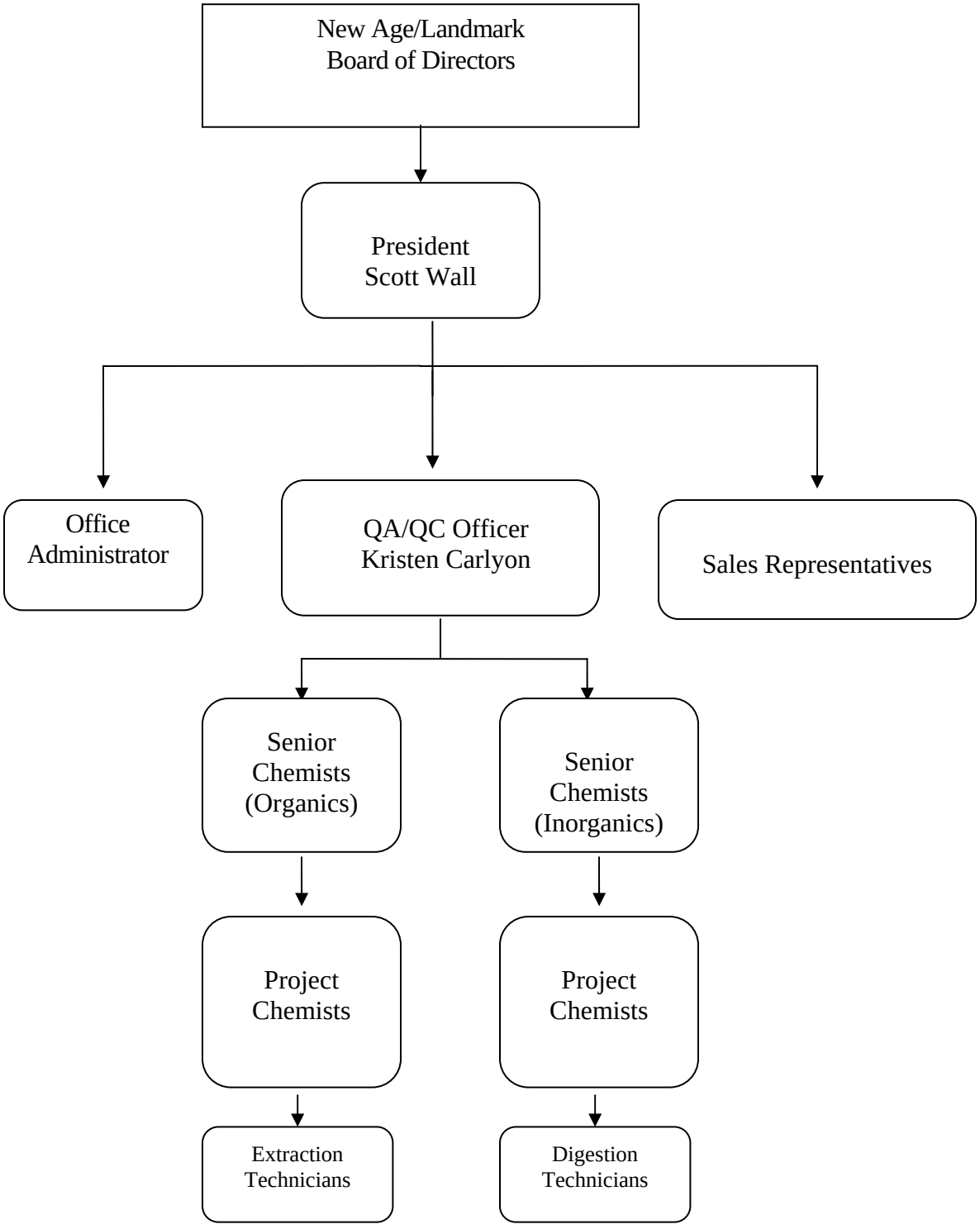
Trip Blanks - A check on sample contamination originating from sample storage, transport, and from ambient site conditions. They are prepared in a laboratory prior to departure, handled in the field as a field sample would be, but not opened in the field.

Water (Reagent, Analyte-Free, or Laboratory Grade) - Distilled or deionized water or Type II reagent water that is free of contaminants that may interfere with the analytical tests in question.

APPENDIX B

APPENDIX C

New Age/Landmark, Inc.
Organization Structure



QUALITY ASSURANCE MANUAL
RECEIPT AND ACKNOWLEDGMENT

I have received a copy of the New Age/Landmark Mobile Laboratories Quality Assurance Manual, dated March, 2003.

The document contains policies and procedures which apply to me and the work I perform. I have read the Quality Assurance Manual, understand the contents of said document, and agree to comply with it during my employment with New Age/Landmark Mobile Laboratories. I further understand that the Quality Assurance Manual may be amended or updated at any time, and that all changes will be communicated to me.

_____ _____
Employee Signature Date

_____
Employee Name (Print)

_____ _____
President Date

PREPARED BY: JMK/SDW
REVISION NO.: 11
APPROVED BY:
DATE: 12/22/04

FIELD PROCEDURE GC/MS-100 VOA

ANALYSIS of VOLATILE ORGANIC COMPOUNDS BY EPA SW-846 METHOD 8260

1. APPLICATION OF METHOD

SW-846 Method 8260B is used to determine volatile organic compounds using a purge-&-trap system coupled with a GC/MS. Chromatographic retention times and unique ions identify compounds of concern. These compounds are quantified by comparing acquired response factors to responses of respective initial calibration response curves. Analysis of samples will be performed in batches of 20 or less field samples. A batch will consist of (at a minimum), a tune, a beginning CCV, followed by a method blank, the field samples, a sample matrix spike and matrix spike duplicate, and a Lab Control Spike (if needed to meet project requirements). All tune evaluations and calibrations cycles are a maximum of 12 hours long. A field duplicate, if requested by the client, is treated like a sample.

2. APPLICABLE MATRICES

This method may be used to analyze various matrices including groundwater, air, wastewater, soil, and sludge.

3. METHOD DETECTION LIMITS

The MDLs were established using procedures given in EPA 40 CFR Part 40, Appendix B. The results are tabulated and the statistical calculations are performed electronically to establish the MDLs and RDLs for each analyte and matrix. MDL results are in table 1.

4. SCOPE AND APPLICATION

Table 2 contains the standard compound list for this method; however, it is also applicable to other compounds, as listed in EPA SW-846 Method 8260.

5. SUMMARY OF METHOD

Volatile compounds are introduced into a gas chromatograph (GC) by a purge and trap unit, using EPA method 5030 or 5035. Samples are purged with Helium directly from water samples, soil-water solutions, or methanol extract-water solutions. The volatile compounds are collected on a sorbant

trap and then desorbed into a capillary column. A temperature program is used to separate the different compounds. A mass spectrometer (MS) interfaces with the GC, such that each compound is identified by the respective ion pattern (see Table 2), and the relative retention time.

6. DEFINITIONS

6.1. **Surrogate**: A compound added to all analyses at a known concentration. Specific recovery requirements are established to monitor the performance of the analysis.

6.2. **Internal standard**: A compound added at a known concentration to all analyses. The internal standard response is compared to the response of target analytes for quantitative analysis by generating relative response factors.

6.3. **Method blank**: A representative clean matrix that is prepared and analyzed like all other samples in the perspective batch. The method blank is used to demonstrate that the system is free of contamination.

6.4. **Matrix Spike**: A sample representative of the batch matrix that is spiked with a known quantity of the compounds of concern. Specific recovery requirements are established to ensure quality performance.

6.5. **Laboratory Control Spike**: A representative clean matrix, spiked with a known quantity of the compounds of concern that is prepared and analyzed like all other samples in the perspective batch. The laboratory control spike demonstrates that the analysis is being performed within acceptable control limits.

6.6. **Initial Calibration**: Five or more calibration standards that are used to generate average response factors. The response factors of samples are compared to initial calibration response factors for quantitation of specific analytes.

6.7. **Continuing Calibration**: A standard analysis performed every 12 hours or less to demonstrate that the initial calibration is still applicable. Specific recovery requirements are established to ensure quality performance.

7. EQUIPMENT & SUPPLIES

- Hewlett Packard 5890GC with a 5970 or 5972 MSD
- Tekmar ALS2016 16-position Autosampler
- Tekmar LSC2000 Purge & Trap Controller
- Computer equipped with Chemstation software
- DB624 30m x 0.25mm ID x1.12 micron film column (or equivalent)
- Disposable purge culture tubes
- 2 x 5-ml gas-tight syringes
- 1 x 25-ml gas-tight syringe
- Assorted microsyringes – 10-, 25-, 100-, 250-, and 500-µl
- Analytical balance accurate to 0.1mg
- Refrigerator with calibrated thermometer
- Dry weight oven with calibrated thermometer
- Spatula

8. REAGENTS & STANDARDS

- Organic-free reagent water
- Methanol, CH_3OH, purge-and-trap grade or equivalent
- Helium ultra pure gas
- Internal standards and surrogates mix @ 2000µg/ml from Accustandard.
- Gaseous analyte mixture standard @ 2000µg/ml from UltraScientific, Accustandard, and ChemService.
- 8260 main mixture standard @ 2000µg/ml from UltraScientific, Accustandard, and ChemService.
- 8260 supplemental mixture standard @ 2000µg/ml from UltraScientific, Accustandard, and ChemService.
- 2-Methyl Naphthalene, MTBE, or any unique project specific standards from ChemService and Accustandard.

9. INTERFERENCES

Volatile organic compounds are common in many laboratory and everyday applications. Therefore, diligence must always be taken to avoid system contamination. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials may release organic compounds which will be concentrated in the trap during the purge operation. Analysis of reagent blanks provides information about the presence and nature of contaminants. If detected, the source of contamination should be identified and eliminated. Subtracting blank values from sample results is not permitted. If results

contain expected contamination, the laboratory should fully explain this in text accompanying the uncorrected data.

9.1. **Methylene Chloride:** Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all sources of methylene chloride otherwise random background levels may result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes can contribute to sample contamination.

9.2. **Carryover:** Contamination may occur when a sample is analyzed immediately after a sample containing high analyte concentrations. To limit carryover all syringes are rinsed between each sample analysis. The 5-ml gas tight syringes are rinsed three times with organic-free reagent water, and the sample dilution syringes are rinsed three times with methanol. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the contamination compounds, freedom from contamination has been established.

10. SAMPLE COLLECTION

The client or the client's representative submits samples and a completed Chain of Custody (COC) form to the field laboratory. Once received, the samples are inspected for labeling accuracy and any abnormalities (headspace, high sediment, etc.) The sample containers are labeled with the appropriate lab ID number and the samples are refrigerated at 4°C (±2°C) until the time of analysis. All individual containers received for AFCEE projects must be identify with a lower case letter at the end of the lab ID to denote container ID.

10.1. **Sample Holding Times:**

10.1.1. Soils

For Method 5035 the standard holding time is 14 days. If methanol preservation is utilized the extract is valid up to 28 days.

10.1.2. Waters

For Method 5030 the standard holding time is 7 days for unpreserved samples, 14 days for samples preserved to pH < 2 with 1:1 (v/v) HCl at time of sampling.

11. PROCEDURE

11.1. **Project Startup:** All equipment is turned on and allowed to equilibrate for optimal performance prior to tuning and calibration. After the instrument has been shutdown it is especially important to let it stabilize before the calibration is checked. Equilibration may take 4 hours or more. Also, when the power is turned off components may reset to a default program. Therefore, the chemist needs to ensure that the correct program is set on all applicable instruments. Prior to any daily use, the proper operating condition of all equipment (balance, oven, sample refrigerator, etc.) needs to be checked.

11.1.1. **Purge and Trap Setup:**

The Tekmar LSC2000 is set-up as follows:

11-minute purge
1-minute dry purge
1-minute desorb at 250°
8-minute bake-out at 260°
Line and valve temperatures are set at 125°
The standby temperature is set for 35°
Desorb preset is set for 245°

Although specific program settings may vary, the program is to be identical for each standard and sample in a given project.

11.1.2. **GC Setup:** Prior to starting the GC/MS, ensure that the column is placed properly within the oven, that the carrier gas is on, and that there is a head pressure reading on the flow controller. After starting the GC/MS, load the Chemstation software from the desktop. The Chemstation software controls all functions of the instrument. From the data analysis screen load the last data acquisition method used and observe the front panel of the GC to ensure that the GC and computer are communicating. Elevate the oven temperature to 100°C and check for leaks.

11.1.3. **Mass Tuning:** From manual tune or diagnostic screen, ensure that the ions 18 (water) and 28 (N_2 from air) are less than 10% the response of ion 69 in the calibration gas. From the manual tune screen, load the current tune values "BFB.U", and observe ions 69 (100%) 131 (35-40%), and 219 (35-40%). If necessary Autotune or manually tune the instrument and save these tune values as "BFB.U". Return to the Instrument control screen, and load the last sequence used. Note the numeration on the final sample analyzed and start with the next sequential number to begin the new sequence. Save the sequence, and the data folder as the current date, and run a blank containing 50ppm of Bromofluorobenzene (BFB). From the data analysis screen load the last data analysis method, and zoom in on the BFB peak. With the right mouse button double-click on the peak to attain one individual scan. At the top of the screen key on "Tuner" and "Evaluate BFB" to determine if the BFB passed the Pass/Fail criteria established by the

method. If no individual scan point produces a Pass response for all criteria, perform a scan averaging by clicking on a scan and while holding the right mouse button, dragging to another scan for an average of all scans within. When a scan or average of scans indicates all ions pass, print out a copy for the daily QC package. This is the beginning of the tune evaluation clock, which must be performed at least once every 12 hours of operation. The passing mass intensity criteria are as follows:

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

11.2. **Daily Instrument Operation:** A standard analysis day consists of; a tune evaluation at least every 12 hours, a continuing calibration verification with each tune evaluation, a method blank with all analyte concentrations less than the corresponding reporting limit, a lab control spike, a spike and spike duplicate for each matrix, and the sample analyses. Unless otherwise specified, all spikes are performed at 50 ppb.
Everyday, prior to any sample analysis, the operating conditions of the instrument must be verified. A Bromofluorobenzene (BFB) tune evaluation must be analyzed and meet the criteria listed in section 11.3. A CCV must follow and meet the acceptance criteria indicated in section 14.6. Alternatively, the CCV and the BFB tune evaluation can be performed in the same analysis. These analyses must be completed before any other can occur. Also, note that the tune evaluation is considered valid for no more than 12 hours. If the tune clock is allowed to expire, a new BFB and CCV must be successfully analyzed before any other analysis can occur.

11.3. **Sample Acquisition:** Sample may be analyzed once an acceptable BFB mass tuning standard, CCV standard, and method blank have been attained. Sample analysis may continue for up to 12 hours from the time that the tuning standard was injected.
To add samples to the sequence table, click on the sequence screen; go to "Sequence" and "Edit Sequence Table". Highlight the last run in the sequence, and click the "Repeat" button. Change the sample name and add all pertinent information into the sample name box or the miscellaneous box. If more than one sample is to be loaded into the sequence repeat, and click the "OK" button when finished.
Analyst judgment is crucial to estimate the amount of contamination prior to analysis. Any

result greater than the highest standard must be diluted and reanalyzed. All waters are to be analyzed undiluted, unless gross contamination is suspected. All soils using methanol preservation are to be run at a 50:1 dilution (100µl into 5ml H_2O) unless gross contamination is expected. Efficient and continuous analysis is imperative. One sample should be purging while another is being analyzed.

11.4. **Sample Analysis:** When a sample is finished running, the file can be loaded from the data acquisition screen. Quantitate the sample by clicking on "Quant" and "Cal/Generate Report to the screen". Then from the "Quant" file, enter "Q-Edit Quant Results" and scroll through observing all peaks. All compounds that are identified should have a primary and a secondary ion present, and the integration should be on the x-axis. Evaluate all responses and report everything above the reporting limit. Line through and initial in ink all results on the chromatogram that are below the reporting limit. Do not use the "Q-Delete" button to remove any compounds. When in doubt about calling a hit, if the ion pattern is similar to the compound of interest, call the hit. If a hit is obviously an artifact of a co-eluting peak do not call it. Never cut or shave a peak. Manual Integration to include tailing is permissible and requires the operator's judgment. If manual integration is necessary, print a copy of the original integration, and a copy of the manual integration. Printing is accomplished in Q-Edit mode. Include both printouts with the quantitation report, and date, initial, and briefly note the reason for the change on the hard copies.
The final sequence must be saved and included in the daily data package. The daily data package is to be placed in a file folder. The batch files will include the following order of paperwork: he daily sequence, the IS report, the MS/MSD report, the tune, the continuing calibration report, and all chromatograms in ascending order. Initial and date any changes on sheets.

11.5. **Analysis Order:** Samples are analyzed in the order received or in the order of customer priority. Unless the client has designated the samples for the MS/MSD, select a sample whose matrix is representative of the batch.

11.6. **Sample Preparation Procedures:**

11.6.1. **Soil Samples**:

Method 5035

11.6.1.1. Aqueous Preparation: Weigh 5 grams of soil into the purge vessel. In a 5-ml airtight syringe add 5-ml reagent grade water. 10µl of internal standard and surrogates are added to the 5-ml syringe. The sample is then purged in the purge vessel.

11.6.1.2. Methanol Preservation: Weigh a 40-ml VOA with 10 ml of Purge and Trap grade methanol inside. Add 10 grams of sample to the preweighed VOA, record

the weight on the sample prep log, and sonicate the sample for 20 minutes. Let any particulate settle and withdraw 100 µl of the extract from the VOA. Add this extract to a gas-tight syringe containing 5ml of organic free water. 10µl of the internal standard/surrogate mix are added to the syringe, and the sample is purged. For Laboratory Control Spikes and Method Blanks a vial of clean sand should be prepped as a sample, and 100µl of this methanol extract should be added prior to the standards. The reporting limit when using this method is typically 50 x the standard reporting limits, although samples with a greater dilution will have correspondingly higher reporting limits.

11.6.2. **Water Samples:**

Method 5030

10µl of combined internal standard/surrogate are added to the sample in the 5-ml airtight syringe. All samples should be run with no dilution, unless the sample contains contamination beyond the calibration range. When gross contamination is suspected, a sample dilution needs to be performed. Using an appropriately sized microsyringe, inject an aliquot of the sample into the gas tight syringe containing exactly 5-ml of organic free water. The size of the aliquot will determine the size of the dilution (For example: 100µl of sample into the 5-ml syringe is a 50 x dilution)

12. CALCULATIONS

12.1. **Water Samples**

$$C(\mu g/L) = R_R \times D$$

12.2. **Soil Samples**

Aqueous Preparation:

$$C(\mu g/Kg) = \frac{R_R \times D}{\%S}$$

Methanol Preservation:

$$C(\mu g/Kg) = \frac{R_R \times V \times D}{W \times \%S}$$

Where:
C = Concentration in sample
R_R = Raw read from instrument (ppb)
D = Dilution factor of sample
%S= Percent Solid
V = Vol. of MeOH in extraction
W = Weight of soil extracted

13. QUALITY CONTROL

13.1. **Reagent Purity:** Accurate records are maintained, noting date received, opening dates, and shelf life for all reagents, solvents and standards used in sample preparation and analysis. Any reagent that either contains interfering compounds or becomes contaminated with interfering compounds must be immediately discarded and replaced with an interference-free lot.

13.2. **Standard Logbook:** The standards preparation logbook is completed when all calibration standards, surrogate spike, and internal standard spike solutions are prepared. The log for volatile standards is kept at the in-house laboratory. The standards preparation logbook includes the following information:

Stock solution lot numbers
Initial and final volumes aliquoted
Solvent and solvent lot number
Preparation date and preparer's initials

13.3. **Evaluation of ICV**: Analyze the ICV immediately after a new initial calibration to verify that the calibration standards used were accurate. The % D of the RF to the initial calibration in the ICV can be no more than ±15%. If the recoveries are not met, the compounds that failed these criteria must be evaluated to determine the reason. Any samples run need to be flagged for any failing compounds.

13.4. **Evaluation of LCS and MS**: An LCS and a MS should be analyzed with every QC batch of 20 samples or less. Target recoveries for the LCS and the MS are ±30%. No action is necessary if the spike recoveries of the MS alone do not meet the target QC limits. Issues such as sample heterogeneousness or matrix interference are likely poor recovery factors.

13.5. **Evaluation of Duplicates:** Every QC batch must have a duplicate analyzed to ensure precision of measure. Most often this will be a matrix spike duplicate, but if a difficult matrix is encountered, a laboratory control spike duplicate (LCSD) or a sample duplicate

may be more applicable. Also, if the project specific QC requires multiple duplicates, the Project Manager or the QC Officer will make a note in the project folder. Target recoveries for all duplicates are ±30% of the original result.

13.6. **Evaluation of Internal Standards:** Internal standard responses and retention times must be within QC limits for all analytical runs. The internal standard response and retention time QC limits are based on the mid-point initial calibration standard for all CCVs, and the corresponding CCV standard for all sample analysis. The response of all internal standards must be within –50% to +100% of the response for the appropriate standard. The internal standard retention time must not differ by more than ±30 seconds. If any analytical run does not meet the internal standard QC criteria, it must be repeated. If upon reanalysis the internal standard response criteria are still not met, then the sample must be diluted until the matrix effect is no longer observed.

13.7. **Evaluation of Surrogates:** Surrogate recoveries must be within QC limits for all blanks, spikes, and samples. Surrogates are spiked at 50ppb unless otherwise specified. The criteria for surrogate recoveries are ±30%. The data must be flagged for any sample not meeting the criteria and the sample must be reanalyzed. If the bias is high and there are no reportable levels of compounds in the sample the rerun is not performed. If neither the original analysis nor the reanalysis of a sample yield surrogate recoveries within control limits, then the original analytical run is reported noting a matrix effect in the comment section of the sample report.

13.8. **Evaluation of Method blank:** Each method blank must demonstrate that the analytical system and reagents used in the analytical procedure are interference-free. Sample analysis can proceed once the analytical system is demonstrated to be interference-free.

13.9. **Evaluation of Linear range:** All sample target compound concentrations must not be greater than highest concentration in the initial calibration. If the high calibration standard concentration is exceeded in a sample analysis, then the sample must be reanalyzed at an appropriate dilution. The sample must be diluted to the highest concentration target compound.

14. CALIBRATION AND STANDARDIZATION

14.1. **Initial Calibration:** Using the sequence and established methods for 8260, run a curve of no less than 5 points. Each level must contain equivalent levels of solvent to negate any interference from the MeOH. The following is a typical curve, but appropriate variances may be made.

Std. Conc. (ppb)	8260 I.S./ Surr. 25µg/ml	8260 Gases. 25µg/ml	8260 Main 25µg/ml	8260 Supplement 25µg/ml	2-Meth. or Specialty 25µg/ml	Added MeOH	Final Vol.
1 ng/ml	50 µl	1 µl	1 µl	1 µl	1 µl	796µl	25-ml
2 ng/ml	50 µl	2 µl	2 µl	2 µl	2 µl	792µl	25-ml
5 ng/ml	50 µl	5 µl	5 µl	5 µl	5 µl	780µl	25-ml
10 ng/ml	50 µl	10 µl	10 µl	10 µl	10 µl	760µl	25-ml
25 ng/ml	10 µl	5 µl	5 µl	5 µl	5 µl	140µl	5-ml
50 ng/ml	10 µl	10 µl	10 µl	10 µl	10 µl	120µl	5-ml
100 ng/ml	10 µl	20 µl	20 µl	20 µl	20 µl	80µl	5-ml
150 ng/ml	10 µl	30 µl	30 µl	30 µl	30 µl	40µl	5-ml
200 ng/ml	10 µl	40 µl	40 µl	40 µl	40 µl	0µl	5-ml

(If specialty standards are needed for a specific project, their stocks will be prepared at 25 ppm and they will be added just as the 2-Methyl Naphthalene.)

Analyze the curve in the data analysis screen. Load the data file from the "File" menu on the top of the screen. Quantitate the data file using "Quant" and "Calibrate and Generate". Observe the validity of the quantitation using "Quant" and "Q-edit Quant Results", watching for correct integration and peak identification. By clearing all calibration responses and points via the "InitCal" menu, the new curve is ready to be entered into the computer. Enter the "InitCal" menu and scroll to the "Update Levels" menu choice. Chose "Add New Level", enter the calibration concentration as the level number, enter the calibration concentration, and the internal standard concentration. Click the "Do Update" button. Once all points are loaded, observe the quality of all component curves in the "Edit Compounds Screen". Observe the average response factors, and time permitting, rerun any single point that is seemingly "not on the curve". Calibration points below the reporting limit of the compound may not be included in the calibration.

The RF is calculated as follows:

$$RF = \frac{A_S \times C_{IS}}{A_{IS} \times C_S}$$

where:

A_S = Peak area (or height) of the analyte or surrogate.
C_{IS} = Peak area (or height) of the internal standard.
C_S = Concentration of the analyte or surrogate.
A_{IS} = Concentration of the internal standard.

14.2. **SPCC'S:** There are 5 System Performance Check Compounds (SPCCs) that are monitored

for minimum response. These SPCCs are indicative of system problems. The average RF for the SPCC cannot be less than the listed minimum RF. If the average RF is below the listed minimum, corrective action must be taken, and a new initial calibration must be run. The SPCCs and their associated minimum RFs are listed below;

Compound	Minimum RF
Chloromethane	0.1
1,1-Dichloroethane	0.1
Bromoform	0.1
Chlorobenzene	0.3
1,1,2,2-Tetrachloroethane	0.3

The RSD is calculated as follows:

$$\%RSD = \frac{SD}{RF_M} \times 100$$

where:

SD = Standard Deviation

RF_M = mean RF for each compound from the initial calibration.

A list of analyte RSDs and response factors (RF) should be accessed through the "InitCal" and "Response Factors to Printer". If linear or non-linear regression is used, the curve plot must be printed.

14.3. **CCC's:** The %RSD of each target compound should be 15% or less. However, for the 6 calibration check compounds (CCCs) the %RSD must be less than or equal to 30%. If the %RSD of any of the CCCs is greater than 30%, then the initial calibration must be reanalyzed. The CCC analytes are:

Vinyl Chloride	1,1-Dichloroethene
Chloroform	1,2-Dichloropropane
Toluene	Ethylbenzene.

14.4. **Initial Calibration Acceptance:** Calibration linearity is accepted when the following conditions are satisfied;

14.4.1. The %RSD for all target compound response factors must be less than or equal to 15%. When all compounds cannot attain the 15% criterion, an average of all compound percentages must be less than or equal to15%.

14.4.2. The %RSD of all CCCs must be less than or equal to 30%.

14.4.3. The average Response Factors of the SPCCs must be greater than or equal to the minimum requirements.

14.4.4. Alternatively, other calibration options are acceptable. Either a linear or quadratic regression may be employed. If linear or quadratic fits are used, the correlation coefficient must be 0.99 or greater.

If any of the criteria are not met corrective action must be taken immediately. When an acceptable initial calibration is attained, click "Save Method", and enter "the date.M". When changes are made to a method, a new method name must be assigned. Furthermore, all analyses in a batch must be analyzed using the same method.

14.5. **Continuing Calibration:** Continuing calibration verification (CCV) must be performed at the beginning of each 12-hour tune period. Prepare and analyze a mid-point (usually 50ppb) standard as described in the initial calibration section.

Calculate the RFs for all target compounds, and compare the results to the average RF from the initial calibration. The % difference (%D) is calculated as follows;

$$\%D = \frac{RF_V - RF_M}{RF_M} \times 100$$

Where:

RF_M = mean RF for each compound from the initial calibration.

RF_V = RF for each compound from the continuing calibration.

14.6. **Continuing Calibration Acceptance:** The CCV is considered acceptable if the following conditions are satisfied;

14.6.1. The RF results of the CCCs must be equal to or less than 20% D.

14.6.2. The average of all RFs must be equal to or less than 15% D.

14.6.3. Alternatively, if a regression analysis is performed, all compounds must be equal to or less than 20% D.

14.6.4. The SPCCs must maintain the minimum relative response factor criteria.

14.6.5. The internal standard (IS) area responses of the CCV must be 50% to 200% of the area responses of the last CCV.

A print record of the CCV report is attained in "ContCal" and "Evaluate Data File as Continuing Calibration to Printer" in the data acquisition screen. If a passing CCV is not attained a new CCV should be run. If the second CCV is unsatisfactory, a new initial calibration must be run.

PREPARED BY: JMK/SDW
REVISION NO.: 11
APPROVED BY:
DATE: 12/22/04

15. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

Data is continually assessed for completeness and accuracy. Data assessment starts with the beginning tune. Ensure that all BFB specs fall within acceptable criteria, and print a tune page. The next step in data assessment is ensuring the CCV meets acceptance criteria. After evaluating the continuing calibration report, print it as prove of calibration validity. Ensure the method blank is free of reportable contamination.

Internal standard responses and surrogate recoveries need to be continuously monitored. To document valid IS and surrogate responses, a QA-QC check report needs to be evaluated at the end of each tune cycle. To complete the data assessment, spikes and duplicates need to be evaluated for acceptance.

Quality Control Check List

Quality Control	Frequency	Criteria
Tune Evaluation	Every twelve hours	1) All BFB Specifications must fall within acceptable ranges.
Initial Calibration	As needed.	1) The average RFs for SPCCs as follows: Chloromethane and 1,1-DCA > 0.10; Bromoform > 0.10; Chlorobenzene and 1,1,2,2-Tetrachloroethane > 0.30.
		2) The RF RSDs ≤ 30% for all CCCs (Vinyl Chloride, 1,1-Dichloroethene, Chloroform, 1,2-Dichloropropane, Toluene, and Ethylbenzene), and the average of all others ≤ 15% (Compounds using a regression calibration are not included in this average).
		3) For compounds using a regression calibration, the correlation coefficient for each curve ≥ 0.99.
Continuing Calibration Check	Daily; prior to analysis.	1) Internal Standard Areas between -50% and +100% of the areas observed in midpoint calibration standard.
		2) The average RFs for SPCCs as follows: Chloromethane and 1,1-DCA ≥ 0.10; Bromoform ≥ 0.10; Chlorobenzene and 1,1,2,2-Tetrachloroethane ≥ 0.30.
		3) The RF % RSD ≤ 20% for all CCCs, and the average of all others ≤ 15 %
Method Blank	Daily; prior to analysis.	1) Surrogate recoveries ± 30%.
		2) Blank is free of target compounds ≥ the reporting LOQ.
Laboratory Control Standard (LCS)	Daily; or once per analytical batch.	1) All project-required analytes recovered ± 30%.
Surrogates	Each sample analysis.	1) Surrogate recoveries ± 30%.
Matrix Spike	Daily; or once per analytical batch.	1) All project-required analytes recovered ± 30%.
Duplicate		2) % RPDs ≤ 30%

16. CORRECTIVE ACTION FOR OUT-OF-CONTROL DATA

The following are appropriate corrective actions to be taken in the event of out-of-control (OOC) data in the field.

16.1. **Tune Evaluation:** If the tune evaluation does not meet the stated criteria, then the analysis must be repeated until an acceptable tune evaluation is attained. Repeated failures usually indicate a problem with the MS acquisition parameters (ion focus, entrance lens, peak widths, etc.). After documenting the original parameter settings, they can be adjusted in manual tune, printed, saved, and the tune repeated. Even small adjustments can drastically affect the way the instrument evaluates relative ion ratios, which may affect the instruments calibration. Notify your supervisor before attempting any manual tune adjustments. The BFB analysis may be repeated as often as is needed providing corrective actions are concurrently being pursued.

16.2. **Initial Calibration:** If the initial calibration does not meet the criteria discussed in section 14.4, low or high curve points may be removed to correct non-linearity. Data point removal will impact the linear range of the affected compound, and may alter either the reporting limit or the upper limit of the curve. A note on the ICAL folder needs to indicate which compounds are operating with a non-standard linear range, and the affective linear range for that compound. The current initial calibration is the actual calibration range, and, regardless of previous performance, any compound beyond that range needs to be rerun.

16.3. **Continuing Calibration:** If the continuing calibration standard fails, it may be repeated up to two more times. The first repeat is to check for an instrumentation anomaly. The second rerun should be performed with a fresh standard vial. If the standard still fails, immediately a new initial calibration must be performed. If there is no time for a full curve, immediately contact the QC Officer for further instructions. These may include; quantiating with qualified data, running a new curve, or even ceasing instrument operation.

16.4. **Method Blank**: If the method blank contains target compounds above the reporting limit, reanalysis is required until a clean system is demonstrated. If concurrent analyses have consistent results, contamination can be assumed, and the appropriate QC qualifier needs to be applied to all affected batch samples.

16.5. **Tune Clock Violation:** Any samples analyzed beyond the12 hours tune clock, will need to be reanalyzed.

16.6. **Hold Time:** Any sample analysis beyond the given hold time needs to be qualified, and have it clearly stated in the comment section of the report.

16.7. **Surrogate Area Failure:** Samples that fail the surrogate recovery criteria must be re-analyzed. Although, if the surrogates are higher than expected, and the samples have no detected analytes, then the results may be reported. If the same non-reportable failure is observed upon reanalysis, matrix interference may be assumed, and both sample results are reported with an explanation in the comment section.

16.8. **IS Area Failure:** Samples that fail the internal standard area criteria must be re-analyzed. Only if an abbreviated list of compounds is being tested, and the affected IS has no associated compounds related to it, is the result reportable. Otherwise, if the same failure is observed upon reanalysis, matrix interference may be assumed, and the sample will need additional dilutions, until the matrix affect is no longer observed. All sample results need to be reported with an explanation in the comment section.

16.9. **Results Beyond the Linear Range:** Samples that attain results beyond the highest calibration standard need to be rerun at an appropriate dilution. Each compound should be reported from the analysis with the smallest dilution in which the result is in the linear range. Any result reported from a secondary dilution should use the "D" qualifier in the QC line of the report. Furthermore, analyses directly after grossly contaminated samples need to be monitored for possible carryover. Any analyte that has results beyond the highest point in the curve will be considered possible contamination in the following sample. All samples affected will be marked with the appropriate qualifier, and will be reanalyzed. Both results should be reported.

17. SAFETY

Safety glasses are required at all times in all laboratories. Protective gloves and lab coats are recommended in the laboratory for all sample preparation. On all projects, chemists need to be aware of, and adhere to the New Age/Landmark Health and Safety Plan, and any site-specific health and safety requirements

18. POLLUTION PREVENTION AND WASTE MANAGEMENT

All samples received and analyzed on-site will be returned to the client's representative for proper disposal. New Age staff is not authorized to take permanent possession or dispose of any samples. **Unless authorized by the client and the President, samples are not to be removed from the project site.** When methanol preservation was used, the extracts are to be brought back to the fixed lab to be disposed of in the appropriate solvent waste barrel in the waste area if the garage.

19. REFERENCES

United States Environmental Protection Agency, "Method 5030B: Purge-and-Trap for Aqueous Samples", Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 2, December 1996.

United States Environmental Protection Agency, "Method 5035: Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples", Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 0, December 1996.

United States Environmental Protection Agency, "Method 8000B: Determinative Chromatographic Separations", Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 2, December 1996.

United States Environmental Protection Agency, "Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectroscopy", Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 2, December 1996.

USACE Interim Chemical Data Quality Management Policy for Hazardous, Toxic, and Radioactive Waste Projects.

PREPARED BY: JMK/SDW
REVISION NO.: 11
APPROVED BY:
DATE: 12/22/04

20. TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

TABLE 1
Method Detection Limits and Reporting Limits

ANALYTES	SOIL MDL	WATER MDL	RL	ANALYTES	SOIL MDL	WATER MDL	RL
Dichlorodifluoromethane	0.33	0.22	5.0	Tetrachloroethene	0.78	0.16	1.0
Chloromethane	0.34	0.12	5.0	1,1,2-Trichloroethane	0.57	0.27	1.0
Vinyl chloride	0.16	0.13	2.0	Dibromochloromethane	0.68	0.31	2.0
Bromomethane	0.50	0.16	5.0	1,3-Dichloropropane	0.69	0.14	1.0
Chloroethane	0.51	0.22	5.0	1,2-Dibromoethane	0.50	0.48	2.0
Trichlorofluoromethane	0.29	0.12	5.0	2-Hexanone	2.90	0.82	20.0
Diethyl Ether	1.50	0.32	20.0	Ethylbenzene	0.31	0.21	1.0
1,1-Dichloroethene	0.37	0.18	1.0	Chlorobenzene	0.18	0.12	1.0
Carbon Disulfide	0.49	0.27	20.0	1,1,1,2-Tetrachlorethane	0.26	0.26	2.0
Methyl Iodide	0.91	0.21	20.0	m & p-Xylene	0.49	0.26	2.0
Allyl Chloride	0.71	0.38	20.0	o-Xylene	0.18	0.21	1.0
Methylene chloride	0.22	0.11	5.0	Styrene	0.14	0.20	1.0
Acetone	3.45	3.36	20.0	Bromoform	1.03	0.54	2.0
Trans-1,2-Dichloroethene	0.16	0.28	1.0	Isopropylbenzene	0.29	0.10	2.0
MTBE	1.71	0.23	5.0	n-Propylbenzene	0.50	0.17	2.0
1,1-Dichloroethane	0.24	0.21	1.0	Bromobenzene	0.24	0.27	2.0
Acrylonitrile	2.83	1.39	20.0	1,1,2,2-Tetrachloroethane	0.77	0.60	2.0
cis-1,2-Dichloroethene	0.30	0.20	1.0	1,2,3-Trichloropropane	0.90	0.23	2.0
2,2-Dichloropropane	0.33	0.16	1.0	2-Chlorotoluene	0.19	0.33	2.0
Bromochloromethane	0.49	0.12	2.0	Trans 1,4 Dichloro-2-Butene	2.37	1.32	20.0
Chloroform	0.23	0.08	1.0	4-Chlorotoluene	0.16	0.22	2.0
1,1,1-Trichloroethane	0.38	0.12	1.0	1,3,5-Trimethylbenzene	0.25	0.18	2.0
2-Butanone (MEK)	2.34	2.10	20.0	tert-Butylbenzene	0.36	0.28	2.0
Carbon tetrachloride	0.30	0.16	1.0	Pentachloroethane	1.30	0.32	20.0
Tetrahydrofuran	3.73	1.94	20.0	1,2,4-Trimethylbenzene	0.28	0.10	2.0
Benzene	0.10	0.11	1.0	sec-Butylbenzene	0.41	0.06	2.0
1,1-Dichloropropene	0.18	0.13	1.0	1,3-Dichlorobenzene	0.27	0.08	2.0
1 Chlorobutane	0.46	0.36	20.0	p-Isopropyltoluene	0.31	0.11	2.0
1,2-Dichloroethane	0.43	0.18	1.0	1,4-Dichlorobenzene	0.26	0.15	2.0
Trichloroethene	0.49	0.22	1.0	1,2-Dichlorobenzene	0.19	0.11	2.0
Dibromomethane	0.71	0.39	2.0	n-Butylbenzene	0.46	0.23	2.0
1,2-Dichloropropane	0.40	0.14	1.0	Hexachloroethane	0.26	0.22	20.0
Bromodichloromethane	0.42	0.15	2.0	1,2-Dibromo-3-chloropropane	0.70	1.47	5.0
cis-1,3-Dichloropropene	0.30	0.12	1.0	Hexachlorobutadiene	0.50	0.55	20.0
Toluene	0.29	0.21	1.0	1,2,4-Trichlorobenzene	0.26	0.42	5.0
Methyl Isobutyl Ketone	2.11	0.28	20.0	Naphthalene	0.77	0.60	5.0
trans-1,3-Dichloropropene	0.36	0.13	1.0	1,2,3-Trichlorobenzene	0.46	0.33	5.0

NOTE: Waters are reported in µg/L, soils are reported in µg/Kg.

PREPARED BY: SDW
REVISION NO.: 1
APPROVED BY:
DATE: 11/10/06

FIELD PROCEDURE GC/MS-112 SVOC

ANALYSIS of PARENT and ALKYLATED POLYNUCLEAR AROMATIC HYDROCARBONS

BY EPA SW-846 METHOD 8270 GC/MS-SIM

1. APPLICABLE MATRICIES:

1.1. This 8270C method is used to determine the concentration of parent and alkylated polynuclear aromatic hydrocarbons in extracts prepared from many types of solid waste matrices, soils, sediments, tissue, oily wastes, TCLP extracts, and water samples.

2. METHOD DETECTION LIMIT:

2.1. The MDLs were established using procedures given in EPA 40 CFR Part 40, Appendix B. The results are tabulated and the statistical calculations are performed electronically to establish the MDLs and RDLs for each analyte and matrix. MDL results are in table 1.

3. SCOPE AND APPLICATION:

3.1. This 8270 method is used to determine the concentration of semi-volatile compounds in extracts prepared from many types of solid waste matrices, soils, TCLP extract, air sampling media and water samples.

3.2. This method is intended to be used to quantitate semi-volatile compounds that are soluble in methylene chloride and capable of being eluted, without derivation, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone.

4. SUMMARY OF THE TEST METHOD

4.1. The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to SW-846 3500 Methods) and, if necessary, sample cleanup procedures (refer to SW-846 3600 Methods).

4.2. The semi-volatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS), operating in select ion monitoring mode.

4.3. Analytes eluted from the capillary column are introduced into the mass spectrometer via a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic calibration standards. Quantitation is accomplished using mean relative response factors from a multi-level calibration curve. Response factors for target analytes and surrogate compounds are calculated relative to their associated internal standard. Alkylated PAHs are assigned the response factors of their unsubstituted parent compounds.

4.4. Daily run batch QC will include (at a minimum) a passing tune, a beginning CCV followed by an instrument blank. A method blank may be substituted for an instrument blank. Tunes and daily calibration cycles are12 hours long. (For Method 625 tunes and daily calibration cycles are 24 hours long. Method 625 is a wastewater method with the same extraction requirements as Method 8270.). The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000. See the appropriate extraction SOP for batch QC requirements

5. DEFINITIONS:

Accuracy - The nearness of a result or the mean of a set of results to the true value. Accuracy is assessed by means of reference samples and percent recoveries.

Aliquot – A measured portion of a sample taken for analysis

Analyte – The chemical element or compound an analyst seeks to determine; the chemical element of interest.

Analytical Batch - The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples that are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition.

Analytical Sample – Any solution or media introduced into an instrument, on which an analysis is performed, excluding instrument calibration, initial calibration verification, initial calibration blank, continuing calibration verification, and continuing calibration blank. The following are all analytical samples: undiluted and diluted samples, predigestion spike samples, duplicate samples, serial dilution samples, analytical spike samples, post digestion spike samples, interference check samples, laboratory control sample, preparation blank, and linear range analysis sample (LRS).

Area – A term used in gas chromatography that indicates the peak area of a compound exiting a chromatographic column. The size or area of the peak is proportional to the amount of analyte in the sample

Bias – A systematic (consistent) error in test results. Bias is expressed as the difference between the population mean and the true or reference value, or as estimated from sample statistics, the difference between the sample average and the reference value.

Blank - A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix; however, a universal blank matrix does not exist for solid samples, and therefore, no matrix is used. There are several types of blanks, which monitor a variety of processes: - A method blank is taken through sample preparation and analysis only. It is a test for contamination in the laboratory procedure. – A storage blank is stored and analyzed with samples at the laboratory. It is a test for contamination in sample storage as well as sample preparation and analysis. – A trip blank is shipped to and from the field with the sample containers. It is not opened in the field and, therefore, provides a test for contamination from sample preservation, site conditions, and transport as well as sample storage, preparation, and analysis. It is most commonly used for volatile organics. – A field blank is opened in the field and tests for contamination from the atmosphere as well as those activities listed under trip blank.

Calibration – The systematic determination of the relationship of the response of the measurement system to the concentration of the analyte of interest. Instrument calibration performed before any samples are analyzed is called continuing calibration. Calibration is also the act of making a scheduled comparison of instrument performance against national standards for instruments which measure physical parameters such as mass, time, and temperature.

Calibration Curve – The graphical relationship between the known values for a series of calibration standards and instrument responses.

Calibration Check Standard - A verification of the ratio of instrument response to analyte amount. A calibration check is done by analyzing a standard solution of known analytes in an appropriate solvent matrix.

Calibration Standard - A material used to quantitate the relationship between the output of a sensor and a property to be measured. Calibration standards should be traceable to Standard Reference Materials (provided by NIST, EPA, or other recognized standards agencies) or a primary standard.

Chain of Custody - Procedures and associated documents designed to trace the custody of a sample from the point of origin to final disposition, with the intent of legally

demonstrating that custody remained intact and that tampering or substitutions were precluded.

Chromatogram - A graph representing the signal output of an instrument (GC or HPLC) which can be used to identify organic chemicals by peak retention time (RT) and to quantitate by peak size.

Check Sample - A blank that has been spiked with the analyte(s) from an independent source in order to monitor the performance of the analytical method. The level of the spike will be at the regulatory action level when applicable. Otherwise, the spike will be at five (5) times the estimate of the quantification limit. The matrix used will be phase-matched with the samples and well characterized, i.e., reagent grade water is appropriate for an aqueous sample.

Coefficient of Variation (Relative Standard Deviation) – A measure of precision (relative dispersion). It is equal to the standard deviation divided by the mean and multiplied by 100 to give a percentage value.

Co-elution – When two organics determined by GC give the same retention time (RT) and cannot be differentiated.

Comparability – Expresses the confidence with which one data set can be compared to another data set measuring the same property. Comparability is assured through the use of established and approved analytical methods, consistency in the basis of analysis (wet weight, volume, etc.) and consistency in reporting units (ppm, ppb, etc.).

Completeness – The amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct normal operations. It is usually expressed as a percentage.

Composite – A sample composed of two or more increments.

Concentration – The amount of chemical (analyte) present per amount of sample. For trace analyses, usually expressed as ppm, ppb, or ppt.

Continuing Calibration - A standard analysis performed every 12 hours or less to demonstrate that the initial calibration is still applicable. Specific recovery requirements are established to ensure quality performance.

Decafluorotriphenylphosphine (DFTPP) – An organic compound utilized in several GC/MS methods to establish proper mass spectral instrument performance for semi-volatile analyses.

Dry Weight – The weight of a sample based on percent solids. Also, the weight of a sample after drying in an oven at a specified temperature.

Equipment Blanks - Aliquots of reagent grade water poured appropriately over or through the sample collection device, collected in a sample container, and returned to the mobile laboratory as a sample. Equipment blanks ensure sampling device cleanliness. For projects involving soil gas analysis, equipment blanks consist of ambient air drawn through the collection equipment.

Environmental or Field Sample - A representative sample of any material (aqueous, nonaqueous, or multimedia) collected from any source for which determination of composition or contamination levels is requested or required. For the purposes of this manual, environmental samples will be classified as follows:

a. Surface Water and Ground Water.

b. Drinking Water - delivered (treated or untreated) water designated as potable water.

c. Water/Wastewater - raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents.

d. Sludge - municipal sludges and industrial sludges.

e. Waste - aqueous and nonaqueous liquid wastes, chemical solids, contaminated soils, and industrial liquid and solid wastes.

Extract – The solution (liquid) remaining after a sample has been contacted with an aqueous solution (for inorganics) or an organic solvent (for organics). The extract, containing the chemical of interest, is then processed and analyzed by AA, ICP, or wet chemical techniques (inorganics and metals) or by GC/MS, or HPLC (organics).

Extraction – The process of isolating chemicals of interest from a sample matrix (e.g., water, soil) when the sample cannot be analyzed directly.

Field Blanks – A blank that is prepared and handled in the field and analyzed in the same manner as its corresponding client samples.

Full Scan – The process of monitoring all of the ions formed when a molecule is bombarded with electrons in the mass spectrometer.

Holding Time – The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

Hydrocarbons – Chemical compounds that consist entirely of carbon and hydrogen.

Initial Calibration – Analysis of a series of analytical standards at different specified concentrations; used to define the linearity and dynamic range of the response of an instrument to the target compounds prior to the analysis of samples.

Instrument Tuning – A technique used in GC/MS procedures to verify that the instrument is properly calibrated to produce reliable mass spectral information.

Internal Standards (IS) – A compound added to every sample or sample extract at a known concentration prior to analysis for the purpose of quantitation.

Injection – Process of introducing a portion of a sample extract into a GC, GC/MS, or HPLC.

Laboratory Control Spike - A representative clean matrix, spiked with a known quantity of the compounds of concern that is prepared and analyzed like all other samples in the perspective batch. The laboratory control spike demonstrates that the analysis is being performed within acceptable control limits.

Library Search – A technique in which an unknown mass spectrum of a compound is compared to the mass spectra of compounds contained in a computer library in an effort to identify the compound. Compounds identified in this manner are referred to as tentatively identified compounds (TICs).

Linear Regression – A statistical method for finding a straight line that best fits a set of two or more data points, thus providing a relationship between two or more variables.

Mass Spectrum – A bar graph showing the relative abundance of the ions produced when sample molecules are bombarded by electrons in a mass spectrometer.

Matrix – the component or substrate that contains the analyte(s) of interest. Examples of matrices are water, soil, sediment, and air. Matrix is not synonymous with phase (liquid or solid).

Matrix Effect – An interference in the measurement of analyte(s) in a sample that is caused by materials in the sample. Matrix effects may cause elevated reporting limits or may prevent the acquisition of acceptable results.

Matrix Spike (MS) – An aliquot of a matrix fortified sample spiked with known quantities of specific compounds and subjected to an entire analytical procedure. The percent recovery for the respective compound(s) is a measure of accuracy.

Matrix/Spike Duplicate (MSD) – A second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

Mean – The average of a set of values.

Median – The middle value of a set of data when the data set is ranked in increasing or decreasing order.

Method Blank – An analytical control consisting of all reagents, which may include internal standards and surrogate standards that are carried through the entire analytical procedure. The method blank is used to define the level of laboratory background contamination. Examples of method blanks are a volume of deionized or distilled laboratory water for water samples, a purified solid matrix for soil/sediment samples, or a generated zero air.

Method Detection Limit (MDL) – The minimum concentration of an analyte that, in a given matrix and with a specific method, can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Method Quantification Limit (MQL) - The minimum concentration of a substance that can be measured with a relative degree of confidence and reported.

Minimum Reportable Concentration (MRC) - The minimum reportable concentration of which any value higher than MRC is reported to the client as annotated on the GC summary sheet. Any value less than MRC is annotated as: <MRC.

PAHs (PNAs)- Polyaromatic hydrocarbons, also called PNAs (polynuclear aromatics). A class of hydrocarbons that contain fused benzene rings. In the Air program, these compounds are frequently referred to as Polycyclic Organic Mater (POM).

Percent Difference- When two independent measurements of the same characteristics are available, it is possible to use the percent difference instead of the coefficient of the variation to measure precision.

Percent Recovery- a measure of accuracy determined from the comparison of a reported spike value to its true spike concentration.

Petroleum Hydrocarbon Fingerprinting- A technique for identifying sources of petroleum products

ppb- Part-per-billion. A unit of measurement that expresses the amount of chemical present ('part') per the amount of sample analyzed ('billion'). For example, a 'ng' (nanogram or one billionth of a gram) per 'g' (gram) of sample is 1ppb. More common units are ug/Kg (micrograms per kilogram for solids) and ug/L (micrograms per liter for liquids)

ppm- part-per-million. A unit of measurement that expresses the amount of chemical present ('part') per the amount of sample analyzed ('million'). For example, a 'ug' (microgram or on millionth of a gram) per 'g' (gram) of sample is 1 ppm. More common units are mg/Kg (milligrams per kilogram for solids) and mg/L (microgram per liter for liquids).

Precision – The reproducibility of an analytical technique, usually measured by analysis of duplicates of duplicate spikes. Precision is usually expressed in terms of relative standard deviation or relative percent difference, but can be expressed in terms of the variance, range, or other statistic.

Practical Quantification Limit (PQL) - The lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

Raw Data- All documentation associated with the original recording of analytical results pertinent to a specific sample or set of samples. This may include laboratory worksheets, calculation forms, instrument-generated output, analyst notes, etc., from sample receipt through final reporting.

Reagent Blank - A reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch.

Reagent Grade - Synonymous term for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

Relative Percent Difference (RPD)- Statistic for evaluating the precision of a replicate set.

Replicate Sample - A sample prepared by dividing it into two or more separate aliquots. Duplicate samples are considered to be two replicates.

Resolution-The degree of separation between peaks elution from a chromatographic column. Sufficient resolution between peaks is required for proper quantitation of unknown analytes.

Response Factor (RF)- A factor derived from the calibration of a compound that is used in the quantitation calculation of sample analytes. A response factor may be derived from an external standard calibration (then called a Calibration Factor) or from an internal standard calibration (then called a Relative Response Factor).

Retention Time- a term used in gas and liquid chromatography describing the time elapsed from sample injection until the specific compound elutes or exits the chromatographic column at the detector. Each compound has a characteristic retention time on a specific column; therefore, this information is used to qualitatively identify the compounds in the sample.

Selected Ion Monitoring (SIM)- A technique in which one or more specific ions are monitored. Because only specific ions are monitored, selected ion monitoring generally provides higher sensitivity than a full scan monitoring. A term applicable only to GC/MS.

Semi-Volatile Organics - Organic chemicals which generally contain six to thirty carbon atoms and are amenable to GC, GC/MS or HPLC analysis.

Solid Waste - Nonliquid , nonsoluble, materials, ranging from municipal garbage to industrial wastes, that contain complex, and sometimes hazardous, substances. Solid wastes include sewage, sludge, agricultural refuse, demolition wastes, mining residues, and even liquids, and gases n containers.

Standard Curve - A curve that plots concentrations of known analyte standard versus the instrument response to the analyte.

Standard Operating Procedure (SOP)- A detailed written description of how a laboratory executes a particular procedure or method, intended to standardize its performance.

Stock Solution- a concentrated solution of analyte(s) or reagent(s) prepared and verified by prescribed procedure(s), and used for preparing working standards or standard solutions.

Subsample- A portion taken from a sample. A laboratory sample may be a subsample of a gross sample; similarly, test portion may be a subsample of a laboratory sample.

Surrogate – Compounds that are added to every blank, sample, LCS, matrix spike, matrix spike duplicate, and standard for most organic analyses. They are used to evaluate analytical efficiency by measuring recovery. Surrogates include brominated,

flouorinated or isotopically labeled compounds that are not expected to be detected in environmental samples.

Target Compounds- Specific compounds that are to be quantified in a sample, based on a standard list of potential compounds.

Traceability- the ability of an analytical standard material used for instrument calibration purposes to be traced to its source. The standards must be traceable via written documentation to sources which produce or sell verified or certified standards, ie., National Institute for Standards and Technology, USEPA, or vendors preparing standards from those sources which they have certified.

Trip Blanks – A sample, usually pure water prepared in the lab, which is taken to the sampling site and then returned with the collected samples. Later analysis will indicate any false positive results in the real samples arising from contamination during shipment.

Water (Reagent, Analyte-Free, or Laboratory Grade) - Distilled or deionized water or Type II reagent water that is free of contaminants that may interfere with the analytical tests in question.

6. INTERFERENCES

6.1. Raw GC/MS data from all blanks, samples and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

6.2. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

6.3. Contaminants coextracted from the sample may cuase matrix interferences. An interference, which is unique to SIM techniques, can arise from the presence of a coeluting non-target compound, which contains the quantification mass ion. This event results in a false positive interference to the reported value for the target compound. This interference is controlled by acquiring data for a confirmation ion, the ratio between the quantification ion and the confirmation ion should agree within +/- 20% of the ratio present in the calibration standard. However, the stability of this ratio decreases as the PQL is approached.

6.4. The presence of a large isolated alkyl homolog is usually indicative of a interference. For example, the presence of a singular apparent C_2-Naphthalene in the absence of other C_2-Naphthalenes or C_3-Naphthalenes is probably an analytical interference. Confirmation may be obtained by the comparison of the SIM scan with a full scan GC/MS analysis.

7. SAFETY:

7.1. The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices shall be followed at all times. Eating, drinking, smoking, or the application of cosmetics is not permitted in the laboratory area. Horseplay of any kind is prohibited. Pipetting by mouth is not permitted. All Personal Protective Equipment (PPE) must be removed before leaving the laboratory area and before entering the employee lounge or eating area. Always wash your hands before leaving the laboratory. All relevant Material Safety Data Sheets (MSDSs) are kept alphabetically in the centrally located file storage, in the common area outside of the Information Technology (IT) offices.

7.2. Approved PPE, which includes Safety Glasses, Gloves and Lab Coats, must be worn at ALL times when handling samples, reagents, chemicals, or when in the vicinity of others handling these items, so that dermal contact is avoided. All standards, reagents and solvents shall be handled under a hood. All flammable solvents must be kept in the flammable storage cabinet, and returned to the cabinet immediately after use. When transporting chemicals, use a secure transporting devise and/or secondary outer container. Chemical storage is properly segregated and adequately ventilated to reduce the possibility of hazardous reactions. Chemical storage in work areas shall be kept to a minimum. Storage on bench tops or other work surfaces, except temporary, is not permitted.

7.3. The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely defined; however, each chemical compound shall be treated as a potential health hazard. From this viewpoint, exposure to chemicals must be reduced to the lowest possible level by whatever means available. All standards and reagents shall be prepared in a hood while using the proper PPE.

7.4. Spilled samples, solvents, reagents, and water must be cleaned up from bench tops, instruments and autosampler surfaces immediately. A spill is considered a quantity of hazardous material if it is two times greater than the normal working volume. Concentrated solvents, acids or bases present a moderate to extreme hazard to the skin and mucous membranes. If contact with the skin occurs, immediately flush with large volumes of water. In the case of acidic/basic spills, the Spill Kit located in each laboratory shall be utilized before attempting to cleanup the spill. Although procedures are designed to minimize the possibility of an accident, all injuries or accidents, regardless of the nature or severity, are to

be reported to the technical director immediately. If an employee discovers a potentially unsafe condition, this must be reported to the technical director immediately. No employee should feel compelled to work in a situation where they do not feel entirely informed, trained, or safe.

7.5. Analytical instrumentation poses the unique possibility of exposure to high voltages. Other than the routine instrument maintenance, as listed in the front of every Instrument Maintenance Logbook, at no time shall an instrument operator attempt to maintenance an instrument alone, or without the proper training, supervision or instruction. Caution must always be used in the presence of moving parts (autosamplers) and hot surfaces injection ports).

7.6. Compressed gas cylinders shall only be moved with the dolly supplied for this specific purpose. The cap must be on the cylinder while it is being moved. The tank must be secured when in its final position. All spent tanks are to be returned in the same manner, and secured until removed by the vendor.

8. EQUIPMENT AND SUPPLIES:

-Hewlett Packard 5890 Series II GC with a 5972 MSD and 7673B tower/auto-sampler/controller
-2mL brown glass crimp top vials, tops and crimper
-Computer equipped with Chemstation software
-Column Rtx5-MS w/Integra Guard 30m.x0.25mmIDx0.25 micron film (or equivalent).

9. REAGENTS AND STANDARDS:

-Methylene Chloride, Pesticide Grade ACS approved.
-Acetone, Pesticide Grade ACS approved
-Hexane, Pesticide Grade ACS approved
-Standards purchased and NIST traceable. Internal standards and surrogates purchased from supplier at 2000ppm
-Recommended Internal Standards are; Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12.
-Recommended surrogates are 2-fluorobiphenyl and p-Terphenyl-d14.
-Primary Standard, a solution of 17 parent PAH’s from Accustandard, or equivalent.
-Secondary Standard, a solution of 17 parent PAH’s from Chemserv, or equivalent.

10. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE:

10.1. Sample collection is not consistent with NAL's scope of operation.

10.2. The client or the client's representative submits samples and a completed Chain of Custody (COC) form to the field laboratory. Once received, the samples are inspected for labeling accuracy and any abnormalities. The sample containers are labeled with the appropriate lab ID number and the samples are refrigerated at 4°C (±2°C) until the time of analysis. All individual containers received for AFCEE projects must be identify with a lower case letter at the end of the lab ID to denote container ID.

10.3. Aqueous samples should be collected in 1L amber glass bottles. Soil samples should be collected in glass 4 oz. jars (sediment samples should be at least 8 oz.). Additional sample (3X) is required if MS/MSD analyses are to be preformed.

10.4. Sample Holding Times:

10.4.1. Soils the standard holding time is 14 days. Once extracted, the extract is valid up to 40 days. Sediment samples if frozen suspend the holding time until removed from freezer.

10.4.2. Waters the standard holding time is 7 days for unpreserved samples. Once extracted, the extract is valid up to 40 days.

11. QUALITY CONTROL:

11.1. Daily QC is vital to the success or failure of a project. In a daily tune cycle, the following must be completed; 12 hour tune, 12 hour CCV, instrument blank (all <RL), up to 20 samples with acceptable surrogate recovery and IS abundance. If more than one acid and one base/neutral surrogate fails have the sample re-extracted if there is enough sample and re-analyze.

11.2. Batch QC is vital to the success or failure of a project. Extraction batch QC must include method blank (all <RL), a set of MS, MSDs of a select number of compounds. A set lab control spike (LCS)/ lab control spike duplicate should also be run to prove matrix affects in the matrix spikes if encountered. It is not necessary that Method blanks, LCS, LCSD, MS and MSDs be run on the same day's tune and calibration cycle as the batch's samples, however no sample data associated with these QC analyses can be reported as complete until QC analyses are run and have passed.

11.3. Internal Standard (IS) responses must always be between –50% and +100% of the IS responses of the previous CCV.

11.4. Surrogate recoveries are usually empirical data. The method publishes the following pass/fail criterion.

11.4.1. Surrogate Compound Water% Recovery Soil/Sediment

2-Fluorobiphenyl	43-136	30-145
p-terphenyl-d14	33-141	18-137

11.5. LCS/LCSD acceptable recoveries QC limits are 40-140% with 50% RSD.

11.6. MS/MSD acceptable recoveries QC limits are 40-140% with 50% RSD. At least one set of spikes must pass the established control limits or the batch must be re-extracted.

12. Standards Preparation

12.1. IS and surrogates are purchased standards @ 2000 ppm):

12.1.1. IS

12.1.1.1. 10µL of IS is added to each 1mL sample and standard prior to injection, resulting in 20ng on column injection.

12.1.2. Surrogates

12.1.2.1. 50µL of surrogate is used in soil, to yield 20ng in the final 5mL extract.

12.1.2.2. 5µL of surrogate is used in water, to yield 10ng in the final 1mL extract.

12.2. Target compound mixes for compounds of concern are usually purchased at 1000ppm or 2000ppm. Aliquots are then taken to produce the 1, 2, 5, 10, 20, and 40ng standards of the 6-point initial calibration. Of course, surrogates are added into that mix and the final aliquot receives 10µL of IS.

13. CALIBRATION AND STANDARDIZATION:

13.1. Prior to the analysis of any standards or samples, the instrument acquisition and process methods must be established. First, the mass spectrometer must be tuned to meet the sensitivity and resolution criteria for PFTBA, then checked against DFTPP. Secondly, this must include the GC parameters and the SIM mode acquisition ion entries into the different SIM acquisition retention time windows. An initial calibration must be analyzed to establish linearity of the instrument.

13.2. PFTBA Manual Tuning

13.2.1. Prior to initial calibration tune the mass spectrometer using PFTBA to maximize the sensitivity of the instrument in the mass range of 35 to 550 amu.

13.2.2. To acquire a PFTBA Tune.

13.2.2.1. Go into “Instrument Control” in the “GC/MS Top Environment” screen.
13.2.2.2. Go to “View” and select “Manual Tune”.
13.2.2.3. Go to “File” and select “Load Tune Values”. Select DFTPP.u file.
13.2.2.4. Go back to “File” and select “Generate Report”. If the profile meets the criteria (m/s 69 1.5 mil, 219 30-60%, 502 1-5%, all with peak widths between .45 and .55) exit to the “Instrument Control” screen.
13.2.2.5. If the PFTBA profile does not meet the criteria, utilize the manual tune parameters to achieve passing sensitivity and resolution. Genrate report and save.

13.3. DFTPP tune evaluation.

13.3.1. Prior to daily analysis the mass spectrometer must be confirmed to still be within tune criteria by analyzing a 50ng/ml DFTPP solution.

13.3.2. The following DFTPP mass intensity criteria must be used:

Mass	**m/e Abundance Criteria**
51	30-60% of 198
68	>2% of 69
70	>2% of 69
127	40-60% of mass 198
197	>1% of mass 198
198	Base peak, 100%
199	5-9% of mass 198
275	10-30% of mass 198
365	<1% of mass 198
441	<.01% but >101% 443
442	<40% of mass 198
443	17-23% of mass 442

13.4. GC Instrument Conditions

13.4.1. Inject an aliquot of 1 to 3 ul (Injection volume is dependent on clients DQOs.) into the capillary column of the gas chromatograph, at the following conditions.

GC Parameter	**Setting**
Injector Temperature	300^{o}C
Initial Oven Temperature	40^{o}C
Initial Hold Time	1 minute
Ramp Rate	6^{o}C/ minute
Final Temperature	290^{o}C
Final Hold Time	18 minutes
Total Run Time	60 minutes
Injection Port Mode	Splitless/Const. Flow
Detector Temperature	280^{o}C

13.4.2. GC conditions may be altered to meet clients DQOs.

13.5. Mass Spectrometer Conditions

13.5.1. The carrier gas from the capillary column is transferred into the ion source of the mass spectrometer. The MS is operated in the SIM mode using appropriate retention time windows to include the quantification and confirmation ions for each PAH as shown in Table 1.

13.6. Data Acquisition Parameters

13.6.1. SIM windows must be set up that are inclusive of the retention times for each target analyte. For each of these windows ion masses are selected to include the quantification and confirmation ions for each parent PAH and Alkyl homolog group. To establish the expected retention time window ranges, the mid-level calibration standard must be analyzed in full scan mode. The resulting full scan analysis will dictate the windows in which the selected ions will be monitored. The table below outlines the windows and the ions that are monitored within each window. Depending on the length of the analytical GC column, the time each window is selectively monitored may vary.

Window Number	Selected Ion Monitored
#1	136, 128, 180, 162, 217, 138, 152, 134, 127, 218, 96, 166, 148, 191, 192
#2	142, 156, 180, 162, 218, 152, 141, 155, 166, 191, 192, 194, 176, 148, 217, 150
#3	164, 162, 168, 194, 184, 154, 153, 139, 170, 183, 156, 155, 152, 169, 176, 180, 218, 191, 192, 217, 182
#4	174, 155, 184, 179, 217, 182, 176, 166, 183, 165, 218, 196, 170, 169, 180, 191, 192
#5	188, 179, 194, 198, 139, 196, 184, 183, 195, 191, 217, 210, 178, 180, 208, 192, 218, 167
#6	191, 194, 198, 206, 234, 101, 240, 211, 192, 195, 212, 207, 235, 217, 210, 202, 208, 226, 220, 216, 218, 234
#7	240, 220, 230, 236, 217, 240, 258, 189, 226, 234, 244, 229, 218, 315, 248, 149, 228, 216, 242, 191, 192, 372, 248
#8	264, 244, 256, 260, 217, 221, 276, 262, 252, 240, 270, 229, 218, 357, 258, 253, 242, 284, 191, 192, 372,248
#9	276, 139, 284, 218, 138, 277, 191, 192, 278, 270, 217

13.6.2. The dwell time for each window should be set to 30, and the resolution should be set to “high”.

13.7. Initial Calibration

13.7.1. Before sample analysis, establish a multi-point response factor calibration curve showing the linear range of the analysis for all target analytes in Table 2. Using the sequence and established method for PAH SIM (aklpahs.m), run a 6-point curve (i.e., 1, 2, 5, 10, 20, and 40ppm). Be sure all compounds are located using "Quant" and "Q-edit Quant results," on menu items. Load via "InitCal" and "UpdateCal" menu choices. Once all points are loaded proceed to observe the quality of all curves, rerun any single point that is not seemingly "on the curve," obtaining the best curve possible while providing good customer service.

13.7.2. Acceptance criteria: 30 % RSD for all target compounds.

13.8. Initial Calibration Verification – ICV

13.8.1. The ICV must follow the initial calibration curve. All PAH's in this verification standard are at a certified concentration. After final processing, calculate the percent recovery of each PAH by using the following calculation:

% Recovery = (raw result / known value) x 100

Acceptance Criteria: All recoveries must be +/-20% of the true values. (Note: For calibration verification recovery calculation the Total of Benzo(b)fluoranthene and Benzo(k)fluoranthene pair is used for evaluation.)

13.9. At the end of the day or during the day the sequence must be saved and included in the daily data package. The daily data package is to be placed in a file folder and firmly attached with clips or other means. The batch files will include the following order of paperwork: daily sequence, the tune, CCV, the method blank, samples, samples in order, re-runs if any and any QC samples run in the 12 hour period. Circle surrogate failures. Initial and date any changes on the data sheets in ink.

13.10. Customer Reporting-see data processing procedure DA-100 in the standard operating procedures.

14. PROCEDURE

14.1. **Sample preparation**

14.1.1. Samples are normally prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	3510, 3535
Soil/Sediment	3540, 3541, 3545, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3550, 3560, 3561

14.1.2. Extract cleanup-Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Analytes of Interest	Methods
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Petroleum waste	3611, 3650

14.2. All equipment is powered up and allowed to reach temperature for optimal performance prior to tuning and calibration (Roughly 4 hours minimum, as Mass Specs are notorious for needing up to three days to stabilize after a source cleaning or major venting). Daily cleanup is necessary to clean the instrument in order to get the instrument to a constant beginning point. This includes a new glass wool filled injection port liner, a clean septum, and cleaned or new gold seal and a cutting of 1-2 inches of column as needed.

14.3. Once the MS is hot, and all auxiliary equipment is turned on, observe ions 18 and 28 against ion 69. These ions should be less than 10% to continue tuning.

14.4. Evaluate the DFTPP tune as described in Section 13.3.

14.5. Continuing Calibration Verification

14.5.1. Following the daily DFTPP tune evaluation a mid-level concentration standard containing all parent PAH compounds must be analyzed and every 12 hours during analysis. All PAH's in this verification standard are at a certified concentration. After final processing, calculate the percent recovery of each PAH by using the calculation in Sec. 13.8.1.

14.5.2. Acceptance Criteria: Compare the CCV resulting response against the average response for the initial calibration for each calibrated PAH, and calculate the % difference (%D). See Section 15.0 for the calculations. The %D for each calibrated PAH must be below 30%. If multiple CCVs are analyzed during or within a single analytical sequence, each CCV must be analyzed within 12 hours of the previous CCV. (Note: For calibration verification recovery calculation the Total of Benzo(b)fluoranthene and Benzo(k)fluoranthene pair is used for evaluation.)

14.6. The sequence labeling is of utmost importance.

14.7. Sequences have spaces for logging in the sample information for every analysis to be done in the order they are inject to the GC. Utmost care is to be taken to insure that sample information is correct and complete and the right bottle is designated vial position on the auto-sampler. The client assigns the sample identification and the lab assigns a lab number (Example: Client sample identification MW-1, Lab number A0001). The sequence name on all paperwork will read: MW-1 (A0001). Additional information is critical to reporting calculations, i.e., soil, water, 1:2 dilution, etc.

14.8. Data acquisition occurs in the Chemstation Offline window "GC/MS Instrument #1," "Instrument Control." All present methods are entitled 103100AP.M (representing mm:dd:yy Alkylated PAH). If in doubt as to the current method (curves), consult the logbook or print out an "Initial Reference Factors" to the screen to observe the last time the initial calibration was updated.

14.9. Once the data file is complete, call up the file, "File," "Load Data File," and quant it by "Quant," "Cal/Generate Report to the screen." Then "Quant," "Q-Edit Quant Results," to observe all peaks. All compounds that are identified should have primary and secondary ions present.

15. DATA ANALYSIS AND CALCULATIONS

15.1. After sample analysis, "Not Reviewed" quantitation reports are generated by the software system. It is expected that situations will arise when the automated quantitation procedures of the chromatographic software provide inappropriate quantitations or integrations. This normally occurs when there is compound co-elution, baseline noise or matrix interference with the priority pollutant PAH compounds. However, with alkylated PAH homolog groups, a range or cluster of peaks, is evaluated and manual integration must be performed for each PAH homolog group or cluster.

15.2. Identification of the priority pollutant PAH compounds is based on gas chromatographic relative retention times (RRTs) from the analysis of the mid-level initial calibration standard. For these compounds, manual quantitations are performed, if necessary, by integrating the area of the quantitation ion or peak. For alkylated PAHs, the homolog groupings (i.e., C3 – Naphthalenes) appear in the extracted ion current profiles (EICPs) as a cluster of isomers. Establish the pattern of each cluster, and the retention time window for the cluster, by analysis of the reference standard. Integrate peaks within the cluster by straight-line integration to the baseline, taking into account background noise in the EICPs. See the most recently generated "detailed" Alkylated PAH reference spectrum hardcopy, that is based on the most recent analysis of the reference standard for a cluster by cluster example of each integration for each alkylated PAH homolog group. Table 1, in Section 23.0, lists the representative ion(s) used for quantitation and confirmation of each parent PAH and aklylated PAH homolog group.**Note:** Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system.

15.3. From EICP of the quantification (primary) mass ions and the confirmatory mass ions, identify all target analytes according to the following criteria:

- The characteristic masses of each analyte of interest should maximize in the same, or within one scan of each other.

- The retention time should fall within $\pm$ 10 seconds of the retention time of the parent PAH from the preceding CCV. **Note:** When evaluation alkyl homolog groups, the retention time of the most intense peak within the group may not have the exact retention time of the most intense peak in the reference standard. Analyst judgment and referral to each Homolog groups' retention time window

is essential for identification. Apply analyst judgment regarding corrective action when this criterion is not met.

- The relative peak heights of the primary ion compared to the confirmation of secondary ion masses for parent compounds should fall within ± 50 percent of the relative intensities of these masses in the reference mass spectrum (i.e., the mid-level of the initial calibration curve and/or the reference standard).

Note: The relative intensities of the primary and secondary ions may vary widely within a given group of alkyl homologs (i.e., C3 –Naphthalenes). Thus, the pattern of each alkyl homolog cluster, and the retention time window for the cluster, will be the primary identification criteria for alkyl homologs. In some instances, a parent compound that does not meet secondary ion confirmation criteria may still be determined to be present in a sample after close inspection of the data by the experienced mass spectrometrist. Supportive data includes the presence of the secondary ion, but ratio value greater than ± 50 percent of the primary ion, which may be caused by an interference of the secondary ion.

15.4. In instances where manual integration has been performed, the analyst must identify such edits or manual procedures by initialing and dating the changes made to the quantitation report. The revised hard copy, printed as a "detailed" report, displaying the manual integration, including an "m" qualifier next to the modified or manually integrated compound(s), shall be included in the raw data for secondary review. These requirements apply to all standards, QC samples, field samples and blanks.

15.5. To calculate the Relative Standard Deviation (RSD) of all target analytes and surrogate compounds for the initial calibration use the formula below. The RSD of each target compound and surrogate must be below 30%. Additionally, use the initial six-point calibration to determine Relative Response Factors (RFF) at each concentration level. Average the RRFs to generate mean RRFs, for quantification of all target analytes and surrogate compounds. The RRFs are based on the internal standard compounds, and are calculated using the formula below. (The RRFs for the CCV are calculated using the same formula.)

RSD = SD/mean RRF x 100

Where:

SD = Standard Deviation between the five points, for the target analyte.

$$\mathbf{RRF_I = (A_C \times C_{IS})/(A_{IS} \times C_C)}$$

Where:

A_C = Area of the quantification ion for the standard compound to be measured.
A_{IS} = Area of the quantification ion for the associated internal standard compound.
C_{IS} = Concentration of the associated internal standard compound.
C_A = Concentration of the standard compound to be measured.

Note: Assign the response factor of the parent compound to the alkyl homolog cluster, unless using an authentic representative isomer(s) for each level of alkylation.

15.6. Calculate the Sample Concentration (C) for each compound by following one of the following formula:

15.6.1. **For Waters:**

C = (R x FV)/V x DF

For Soils/Sediments:

C = (R x FV)/(W x %S) x DF

Where:

R = Raw result from chemstation quantification.
FV= Final volume of extract solvent after concentration.
V = Volume of aqueous sample used in sample preparation.
W = Weight of sample used in sample preparation.
%S = % solid of sample extracted.
DF = Dilution Factor of fraction originally spiked with IS.

Report all Alkyl homologs as totals (i.e. Total Naphthalene - C_1, Total Naphthalene - C_2).

15.7. If the response factor of any target compound in a sample exceeds the linear range, as defined in the initial calibration in Section 13.0, dilute the extract so that the concentrations of all target compounds fall within the range of the calibration curve. If the response of any target compound in a sample exceeds the MDL but is below the reporting limit (RL), qualify the reported concentration with a “J”. If any target compound is found in the method Blank and in the associated samples, exceeding the RL qualify the reported concentration with a “B”.

15.8. All results must be reported to two significant figures. All solids including soils, sediments, and sludges must be reported on a dry-weight basis. Tissue

results may be reported in wet-weight depending upon client request. Petroleum results are reported "as received" or on a wet-weight basis.

15.9. The laboratory generates two types of data packages: "Commercial" for routine projects, and "Full Deliverable" or "CLP-like" for fully data validated projects. A Commercial package consists of sample results and the associated method blank and LCS results. A Full Deliverable package includes all sample results, all preparation and instrumental QC results and the associated supporting raw data. Check the "Report Type" on the project folder to ensure all required deliverables are included. A secondary review is performed on all data.

15.10. Procedures for data and record management must adhere to the Quality Assurance Manual; other subordinate documents covering record keeping, the Document Control SOP, and all records shall be stored in such a manner as to be safe and accessible for at least 5 years.

15.11. Laboratory notebooks are designed to accommodate the specific analysis. Instrument printouts are used to document run sequences, and each daily sequence printout is filed in a three-ring notebook. Each page is numbered as it is generated each day the instrument is operated. If a sample required re-analysis or re-extraction for any reason, a notation is made next to the sample entry on the sequence log. After one month of sample analysis, the sequence run log is permanently bound, assigned an internal ID number, and filed accordingly. Such files shall be archived so as to remain available for at least 5 - years. All laboratory notebooks must follow the specifications in the *Laboratory Notebook Usage* SOP, G-009, and all record keeping and document control practices.

15.12. Electronic records: All data files from computers, attached to instruments, shall be backed up daily onto the proper directory on the server. The backups shall be stored so as to be accessible for 5 years. Movement of the data files to the server is the responsibility of the primary analyst. Server backup and storage is the responsibility of the IT department.

16. METHOD PERFORMANCE:

16.1. Initial Demonstration of Proficiency (IDP) is determined by every new analyst during training, and before actual sample analysis. The IDP consists of the preparation and /or analysis of four replicate samples spiked at approximately 10X the Alkylated PAH-SIM MDL. This process ensures the competency of the individual analysts.

16.1.1 The following information needs to be supplied to the QA Manager for reporting and acceptance of the Alkylated PAH-SIM IDP: The *Training Checklist* must be completed by the trainer and

the analyst, and supplied with all of the supporting raw data including, calibration standards, and method blanks in order to reconstruct and validate these analyses. The QA Manager will enter the information on to the individual employee spreadsheet. The following black ID, the four replicate file IDs, mean recovery, standard deviation and a comparison against the control limits, for precision and accuracy. The aqueous and solid limits for precision are 40%-140% recovery and for accuracy are 50% RPD.

16.1.2 If any parameter does not meet the control limits, the QA Manager will notify the Section Head and the analyst. The analyst must repeat the IDP until all criteria are met.

16.1.3 Upon successful completion of the IDP, the IDP Certificate Statement form will be completed by the analyst, and signed-off by the Technical Director and QA/QC Officer.

17. POLLUTION PREVENTION AND WASTE MANAGEMENT

17.1. All samples received and analyzed on-site will be returned to the client's representative for proper disposal. New Age staff is not authorized to take permanent possession or dispose of any samples. **Unless authorized by the client and the President, samples are not to be removed from the project site.** When methanol preservation was used, the extracts are to be brought back to the fixed lab to be disposed of in the appropriate solvent waste barrel in the waste area if the garage.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES:

18.1. Data is continually assessed for completeness and accuracy. Data assessment starts with the beginning tune. Ensure that all DFTPP specs fall within acceptable criteria, and print a tune page. The next step in data assessment is ensuring the CCV meets acceptance criteria. After evaluating the continuing calibration report, print it as prove of calibration validity. Ensure the method blank is free of reportable contamination.

18.2. Internal standard responses and surrogate recoveries need to be continuously monitored. To document valid IS and surrogate responses, a QA-QC check report needs to be evaluated at the end of each tune cycle. To complete the data assessment, spikes and duplicates need to be evaluated for acceptance.

Quality Control Check List

Quality Control	Frequency	Criteria
Tune Evaluation	Every twelve hours	1) All DFTPP Specifications must fall within acceptable ranges.
Initial Calibration	As needed.	30% RSD for all target analytes with exception for 10% of target analytes to be >30%, but <40%.
Initial Calibration Verification	Following each Initial Calibration	+/-20% recovery of the true values
Continuing Calibration Check	Daily; prior to analysis.	≤30% D for all target analytes with exception for 10% of target analytes to be >30%, but <40%.
Method Blank	Once per analytical batch.	≤ 5X the MDL
Laboratory Control Standard (LCS)	Once per analytical batch.	40-140% Rec. for all Target analytes
Surrogates	Each sample analysis.	30% - 150% recovery
Matrix Spike/Matrix Spike Duplicate	Once per analytical batch.	40-140% Rec. for all Target analytes, 50% RPD between the duplicates.
Sample Duplicate		50% RPD between the duplicates.
Internal Standards		50% - 200% of the previous CCV
Reference Standards		+/-35%D or 65%-135% recovery

19. CORRECTIVE ACTION FOR OUT-OF-CONTROL The following are appropriate corrective actions to be taken in the event of out-of-control (OOC) data in the field.

19.1. **Tune Evaluation:** If the tune evaluation does not meet the stated criteria, then the analysis must be repeated until an acceptable tune evaluation is attained. Repeated failures usually indicate a problem with the MS acquisition parameters (ion focus, entrance lens, peak widths, etc.). After documenting the original parameter settings, they can be adjusted in manual tune, printed, saved, and the tune repeated. Even small adjustments can drastically affect the way the instrument evaluates relative ion ratios, which may affect the instruments calibration. Notify your supervisor before attempting any manual tune adjustments. The DFTPP analysis may be repeated as often as is needed providing corrective actions are concurrently being pursued.

19.2. **Initial Calibration:** If the initial calibration does not meet the criteria discussed in section 13.7, low or high curve points may be removed to correct non-linearity. Data point removal will impact the linear range of the affected compound, and may alter either the reporting limit or the upper limit of the curve. A note on the ICAL folder needs to indicate which compounds are

operating with a non-standard linear range, and the affective linear range for that compound. The current initial calibration is the actual calibration range, and, regardless of previous performance, any compound beyond that range needs to be rerun.

19.3. **Continuing Calibration:** If the continuing calibration standard fails, it may be repeated up to two more times. The first repeat is to check for an instrumentation anomaly. The second rerun should be performed with a fresh standard vial. If the standard still fails, immediately a new initial calibration must be performed. If there is no time for a full curve, immediately contact the QC Officer for further instructions. These may include; quantiating with qualified data, running a new curve, or even ceasing instrument operation.

19.4. **Method Blank**: If the method blank contains target compounds above the reporting limit, reanalysis is required until a clean system is demonstrated. If concurrent analyses have consistent results, contamination can be assumed, and the appropriate QC qualifier needs to be applied to all affected batch samples.

19.5. **Tune Clock Violation:** Any samples analyzed beyond the12 hours tune clock, will need to be reanalyzed.

19.6. **Hold Time:** Any sample analysis beyond the given hold time needs to be qualified, and have it clearly stated in the comment section of the report.

19.7. **Surrogate Area Failure:** Samples that fail the surrogate recovery criteria must be re-analyzed. Although, if the surrogates are higher than expected, and the samples have no detected analytes, then the results may be reported. If the same non-reportable failure is observed upon reanalysis, matrix interference may be assumed, and both sample results are reported with an explanation in the comment section.

19.8. **IS Area Failure:** Samples that fail the internal standard area criteria must be re-analyzed. Only if an abbreviated list of compounds is being tested, and the affected IS has no associated compounds related to it, is the result reportable. Otherwise, if the same failure is observed upon reanalysis, matrix interference may be assumed, and the sample will need additional dilutions, until the matrix affect is no longer observed. All sample results need to be reported with an explanation in the comment section.

19.9. **Results Beyond the Linear Range:** Samples that attain results beyond the highest calibration standard need to be rerun at an appropriate dilution. Each compound should be reported from the analysis with the smallest dilution in which the result is in the linear range. Any result reported from a secondary dilution should use the “D” qualifier in the QC line of the report. Furthermore, analyses directly after grossly contaminated samples need to be monitored for possible carryover. Any analyte that has results beyond the highest point in the curve will be considered possible contamination in the following sample. All samples affected will be marked with the appropriate qualifier, and will be reanalyzed. Both results should be reported.

20. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL DATA:

21. REFERENCES:

United States Environmental Protection Agency, "Method 8000B: Determinative Chromatographic Separations", Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 2, December 1996.

United States Environmental Protection Agency, "Method 8270C: Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectroscopy", Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 2, December 1996.

USACE Interim Chemical Data Quality Management Policy for Hazardous, Toxic, and Radioactive Waste Projects.

22. TABLES/DIAGRAMS

22.1. **Water Method Detection Limits** MDLs and RLs are determined for each "parent" PAH only. RLs for Alkyl PAHs are based on the associated parent PAH

Analyte	Spike Conc,	MDL	RDL	Units
2-METHYLNAPHTHALENE	2.5	0.30	5.00	ug/L
ACENAPHTHENE	2.5	0.35	5.00	ug/L
ACENAPHTHYLENE	2.5	0.42	5.00	ug/L
ANTHRACENE	2.5	0.51	5.00	ug/L
BENZO(A)ANTHRACENE	2.5	0.38	5.00	ug/L
BENZO(a)PYRENE	2.5	0.45	5.00	ug/L
BENZO(b)FLUORANTHENE	2.5	0.65	5.00	ug/L
BENZO(k)FLUORANTHENE	2.5	0.60	5.00	ug/L
CHRYSENE	2.5	0.65	5.00	ug/L
DIBENZO(a,h)ANTHRACENE	2.5	0.38	5.00	ug/L
DIBENZO(g,h,i)PERYLENE	2.5	0.47	5.00	ug/L
FLUORENE	2.5	0.35	5.00	ug/L
INDENO(1,2,3-cd)PYRENE	2.5	0.34	5.00	ug/L
NAPHTHALENE	2.5	0.23	5.00	ug/L
PHENATHRENE	2.5	0.43	5.00	ug/L
PYRENE	2.5	0.51	5.00	ug/L

22.2. **Soil/Sediment Method Detection Limits** MDLs and RLs are determined for each "parent" PAH only. RLs for Alkyl PAHs are based on the associated parent PAH

Analyte	Spike Conc,	MDL	RDL	Units
2-METHYLNAPHTHALENE	2.5	0.39	100	ug/Kg
ACENAPHTHENE	2.5	0.37	100	ug/Kg
ACENAPHTHYLENE	2.5	0.52	100	ug/Kg
ANTHRACENE	2.5	0.54	100	ug/Kg
BENZO(A)ANTHRACENE	2.5	0.48	100	ug/Kg
BENZO(a)PYRENE	2.5	0.47	100	ug/Kg
BENZO(b)FLUORANTHENE	2.5	0.55	100	ug/Kg
BENZO(k)FLUORANTHENE	2.5	0.67	100	ug/Kg
CHRYSENE	2.5	0.55	100	ug/Kg
DIBENZO(a,h)ANTHRACENE	2.5	0.36	100	ug/Kg
DIBENZO(g,h,i)PERYLENE	2.5	0.57	100	ug/Kg
FLUORENE	2.5	0.45	100	ug/Kg
INDENO(1,2,3-cd)PYRENE	2.5	0.44	100	ug/Kg
NAPHTHALENE	2.5	0.34	100	ug/Kg
PHENATHRENE	2.5	0.53	100	ug/Kg
PYRENE	2.5	0.53	100	ug/Kg

PREPARED BY: SDW/KAC
REVISION NO.: 6
APPROVED BY:
DATE: 5/17/02

FIELD PROCEDURE GC/MS-110 SVOC

ANALYSIS of SEMI-VOLATILE COMPOUNDS BY EPA SW-846 METHOD 8270

1.0 SCOPE AND APPLICATION:

1.1 This 8270 method is used to determine the concentration of semi-volatile compounds in extracts prepared from many types of solid waste matrices, soils, TCLP extracts, air sampling media, and water samples.

1.2 This method is intended to be used to quantitate semi-volatile compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone.

2.0 SUMMARY OF METHOD:

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Method 3500) and, if necessary, sample cleanup procedures (refer to Method 3600).

2.2 The semi-volatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS), connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.4 Daily run batch QC will include (at a minimum) a passing tune, a beginning CCV followed by an instrument blank. A method blank may be substituted for an instrument blank. Tunes and daily calibration cycles are12 hours long. (For Method 625 tunes and daily calibration cycles are 24 hours long. Method 625 is a wastewater method with the same extraction requirements as Method 8270.). The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000. See the appropriate extraction SOP for batch QC requirements.

PREPARED BY: SDW/KAC
REVISION NO.: 6
APPROVED BY:
DATE: 5/17/02

3.0 INTERFERENCE'S:

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

4.0 EQUIPMENT:

- Hewlett Packard 5890 Series II GC with a 5972 MSD and 7673B tower/auto-sampler/controller
- 2 mL brown glass crimp top vials, tops, and crimper
- Computer equipped with Chemstation software
- Column Rtx5-MS w/Integra Guard 30m. x 0.25mmID x 0.25 micron film (or equivalent)

5.0 REAGENTS:

- Pesticide Grade Methylene Chloride
- Standards purchased and NIST traceable. Internal standards and surrogates purchased from supplier at 2000 ppm
- Recommended Internal Standards are: 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12. Subsets of these are used for PNAs and Pesticides.
- Recommended surrogates are Phenol-d6, 2-fluorophenol, 2,4,6-Tribromophenol, Nitrobenzene-d5, 2-fluorobiphenyl and p-Terphenyl-d14. Subsets are permitted for shortened lists (i.e. PNAs, pesticides).
- Helium ultra pure gas

6.0 PROCEDURE:

6.1 Sample preparation

6.1.1 Samples are normally prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Air	3542

Water	3510, 3535
Soil/sediment	3540, 3541, 3545, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3550, 3560, 3580

6.1.2 Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Analytes of Interest	Methods
Aniline & aniline derivatives	3620
Phenols	3630, 3640, 8041 a
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides/PCBs	3610, 3620, 3630, 3660, 3665 Nitroaromatics/cyclic ketones 3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All BNA priority pollutants	3640
Air/Vapor Samples	NIOSH 5506/5515 (see Sample Preparation

6.2 All equipment is powered up and allowed to reach temperature for optimal performance prior to tuning and calibration. (Roughly 4 hours minimum, as Mass Specs are notorious for needing up to three days to stabilize after a source cleaning or major venting). Daily cleanup is necessary to clean the instrument in order to get the instrument to a constant beginning point. This includes a new glass wool filled injection port liner, a clean septum, a cleaned or new gold seal, and a cutting of 1-2 inches of column. Daily cleaning is essential.

6.3 Once the mass spectrograph is hot, and all auxiliary equipment is on, observe ions 18 and 28 against 69 ion. These ions should be less than 10% to continue tuning. Use the Chemstation Software to Autotune and manually tune the instrument to ions 69 (100%) 131 (35-40%), 219 (35-40%), and 502 (0.8-1.2%) Once achieved use a sequence to do a 2μL injection of 50 ppm DFTPP (inclusive of 4,4-DDT, pentachlorophenol, and benzidene) via direct inject. A tune must be done every 12 hours at the beginning of the run cycle.

6.4 After the DFTPP emerges and using the Chemstation DFTPPDI.M method determine if the DFTPP passed the Pass/Fail criterion established by the method and in the Method itself. Key on a scan, and call up “Tuner”, “Evaluate DFTPP”, “Eval. To Screen”. Once a scan or average of several scans indicates all ions pass, print out a copy for the daily QC package.

6.5 Once a curve is established, a tune, a CCV, and a blank must be run every twelve hours prior to samples being analyzed. Always do a daily cleanup. (NOTE: Method 625 CCV pass/fail is listed on page 212 of 40 CFR, Chapter 1 (7-1-98 Edition).

6.6 The sequence labeling is of utmost importance.

6.6.1 Sequences have spaces for logging in the sample information for every analysis to be done in the order they are injected to the GC. Utmost care is to be taken to insure that sample information is correct and complete and the right bottle is in the designated vial position on the autosampler. The client assigns the sample identification and the lab assigns a lab number. (Example: Client sample identification MW-1, Lab number A0001.) The sequence name on all paperwork will read: MW-1 (A0001). Additional information is critical to reporting calculations, i.e., soil, water, 1:2 Dilution, etc.

6.7 Data acquisition occurs in the Chemstation Offline window “GC/MS Instrument #1””Instrument Control”. All present methods are entitled 103100.M (representing mm: dd: yy). If in doubt as to the current method (curves), consult the logbook or print out an “Initial Reference Factors to the Screen” to observe the last time the initial calibration was updated. All samples are quantified using at least a 5-point Cal Average response factor. Daily Continuing Cal Verifications (CCVs) are required daily, but are not used as single point calibration curves for quantifying. Print out continuing calibration evaluation report.

6.8 Once the data file is complete, call up the file, “File”, “Load Data File”, and quant it by “Quant”, “Cal/Generate Report to the screen”. Then “Quant”, “Q-Edit Quant Results”, to observe all peaks. All compounds that are identified should have primary and secondary ions present.

6.9 Evaluate all hits for compounds of concern that are below the reporting limits, or has only one ion, or is simply noise. If in doubt about calling a hit or not, if the hit is < 1ppb, if both primary or secondary ions, or if a hit is obviously an artifact of a co-eluting peak manually line through the result (in ink), initial, and date. (In duplicate samples, all hits above 1 ppb should duplicate) **NEVER CUT OR SHAVE PEAKS**. Manual Integration to include tailing is permissible and requires operator judgement.

7.0 CALIBRATION

7.1 Using the sequence and established methods for SVOC, run a 6-point curve (i.e., 1, 5, 10, 20, 50, and 100 ppm). For Pesticides use 1, 2, 5, 8, 10, and 15 ppm levels. See section 7.5 for instructions for making standards. Be sure all compounds are located using “Quant” and “Q-edit Quant Results”, on menu items. Load via “InitCal” and “Update Cal” menu choices. Once all points are loaded, proceed to observe the quality of all curves, rerun any single point that is not seemingly "on the

curve", obtaining the best curve possible while providing good customer service. For a subset of 8270, when all CCCs and SPCCs are not included, curves should be less than 20% RSD. If the RSD of the calibration or response factors is greater than 20% over the calibration range, then linearity through the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that does not pass through the origin with a correlation coefficient of .99 or better. If this criteria cannot be attained refer to SW-846 Method 8000B Section 7.5.2. For 8270 long list the calibration pass/fail criterion is as follows:

7.1.1 There are 14 calibration check compounds (CCCs):

Base/Neutral fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2.4.6-Trichlorophenol
Benzo (a) pyrene	

These must be < 30% RSD on an Initial calibration and < 20% on a CCV. All other compounds or the average of all other compounds of interest should be < 15%. The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.

7.2 Daily GC/MS calibration; a mid-level concentration standard containing all compounds must be performed every 12 hours during analysis at the beginning of the run cycle. Compare those response factors to the average response factors of the Initial Cal, using the "Update Cont. Cal" menu and "Print Con. Cal. To Printer", to determine if the pass/fail of the daily CCV.

7.2.1 There are 4 System Performance Check Compounds (SPCCs) and their minimum relative response factors must be .050 on the Initial Cal and Continual Cal checks. They are:

N-Nitroso-di-n-propylamine	Hexachlorocyclopentadiene
2,4-Dinitrophenol	4-Nitrophenol

7.3 At the end of the day or during the day the sequence must be saved and included in the daily data package. The daily data package is to be placed in a file folder and firmly attached with clips or

other means. The batch files will include the following order of paperwork: daily sequence, the tune, CCV, the method blank, samples in order, reruns if any, and any QC samples run in the 12 hour period. Circle surrogate failures. Initial and date any changes on data sheets in ink.

7.4 Customer Reporting – see Data Processing Procedure DA-100 in the Standard Operating Procedures.

8.0 QUALITY CONTROL

8.1 Daily QC is vital to the success or failure of a project. In a daily tune cycle, the following must be completed; a daily tune, daily CCV, method blank (all < RL), up to 20 samples (all surrogates pass), and a set of MS, MSDs of a select number of compounds. A lab control spike (LCS) can also be run to prove matrix affects in the matrix spikes. All acquisition should be done within a 12-hour period (a 24-hour period for Method 625). (Method Blanks, LCS, MS and MSDs can be run the next day's tune and calibration cycle, however no sample data associated with these QC analyses can be reported as complete until QC analyses are run and have passed). If more that one acid and one base/neutral surrogate fails, have the sample re-extracted if there is enough sample and re-analyze.

8.2 Internal Standard (IS) responses must always be between –50% and +100% of the IS responses of the previous CCV.

8.3 Surrogate recoveries are usually empirical data. The method publishes the following pass/fail criterion:

8.3.1

Surrogate Compound	Water % Recovery	Soil/Sediment
Nitrobenzene-d5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-terphenyl-d14	33-141	18-137
phenol-d6	10-94	24-113
2-fluorophenol	21-100	25-121
2,4,6-tribromophenol	10-123	19-122

8.4 LCS/ LCSD recoveries are generally 70-130% with 20% RSD (unless a control chart has been established indicating otherwise).

8.5 MS/MSD recoveries are generally 70-130% with 20% RSD (unless a control chart has been established indicating otherwise). At least one set of spikes must pass the established control limits or the batch must be reextracted.

(NOTE: Method 625 MS, MSD pass/fail criterion is listed on page 212 of 40 CFR, Chapter 1 (7-1-98 Edition) "Range for P1 P2 (Percent)". All compounds of interest must be spiked for Method 625.)

8.6 Standards Preparation.

8.6.1 IS and surrogates are purchased standards @ 2000 ppm):
8.6.1.1 IS
8.6.1.1.1 10 uL of IS is added to each 1mL sample and standard prior to injection, resulting in a 20 ng on column injection.
8.6.1.2 Surrogates
8.6.1.2.1 50 uL of surrogate is used in soil, to yield 20 ng in the final 5 mL extract.
8.6.1.2.2 5 uL of surrogate is used in water, to yield 10 ng in the final 1 mL extract.

8.6.2 Mixes for compounds of concern are usually purchased at 1000 ppm or 2000 ppm. Aliquots are then taken to produce the 1, 5, 10, 20,50, and100 ng of the 6-point initial calibration. Of course, surrogates are added into that mix, and the final aliquot receives 10 µL of IS.

9.0 CALCULATIONS:

9.1 For Waters:
Read (mg/L) x (final extract volume (mL)/initial sample volume (mL)) x 1000 µg/mg = concentration in sample (µg/L)

9.2 For Soils:

$$\text{Read (mg/kg)} \times \frac{\text{final extract volume (mL)}}{\text{Sample weight (g) x dry wt.}} \times 1000\ \mu g/mg = \text{conc. in sample } (\mu g/kg)$$

PREPARED BY: SDW/KAC
REVISION NO.: 6
APPROVED BY:
DATE: 5/17/02

EPA 8270 Quality Control Check List

Quality Control	Frequency	Criteria
Tune Evaluation	Every twelve hours of run time. (every 24 hrs for method 625)	1) All DFTPP Specifications must fall within acceptable ranges.
Initial Calibration	As needed.	1) System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, and 4-nitrophenol. The minimum average RF for these must be 0.050.
		2) The RF RSDs $\leq$ 30% for CCCs, and the average of all others $\leq$ 15%.
		3) Regression coefficients must be $\geq$ .99.
Continuing Calibration Check	Daily; prior to analysis.	1) Internal Standard Areas between -50% and +100% of the areas observed in last CCC.
		2) The % RSD $\leq$ 20%.
Method Blank	Daily; prior to analysis.	1) Surrogate recoveries are as follows: **Acids**: Phenol-d6 and 2-Fluorophenol $\geq$ 25% and $\leq$125%, and 2,4,6-Tribromophenol > 50% and <125%; **Base/Neutrals**: Nitrobenzene-d5, 2-Fluorobiphenyl, and p-Terphenyl-d14 $\geq$ 50% and $\leq$125%.
		2) Blank is free of target compounds $\geq$ the reporting LOQ.
Laboratory Control Standard (LCS)	Daily; or once per analytical batch.	1) All project required analytes recovered within 50-125%.
Surrogates	Each sample analysis.	1) Surrogate recoveries are as follows: **Acids**: Phenol-d6 and 2-Fluorophenol $\geq$ 25% and $\leq$125%, and 2,4,6-Tribromophenol > 50% and <125%; **Base/Neutrals**: Nitrobenzene-d5, 2-Fluorobiphenyl, and p-Terphenyl-d14 $\geq$ 50% and $\leq$125%.
Matrix Spike/Matrix Spike Duplicate	Daily; or once per analytical batch.	1) All project required analytes recovered within 50-125%.
		2) % RPDs $\leq$ 20%

PREPARED BY: DMS
REVISION NO.: 0
APPROVED BY: _____
DATE: 03/24/04

FIELD PROCEDURE ICP-MS-001

ANALYSIS of METALS by ICP-MS BY EPA SW-846 METHOD 6020

1. APPLICATION OF METHOD

This method describes the analysis of metals and some nonmetals using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). All matrices, excluding filtered groundwater samples or water samples with a turbidity less than 1, but including groundwater, aqueous samples, TCLP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis (Refer to SOPs regarding 3010, 3050, and 3060). For a discussion of common interferences and methods of correcting for them, as well as for a list of elements with their expected detection levels for which this method is applicable, please refer directly to EPA SW-846 Method 6020.

2. APPLICABLE MATRICES

This method may be used to analyze various matrices including; groundwater, air, wastewater, soils, and sludges.

3. INSTRUMENT DETECTION LIMITS

The IDLs were established using procedures given in SW-846 Method 6020. The results are tabulated and the statistical calculations are performed electronically to establish the IDLs. Refer to Table 1 for current IDLs and RLs.

4. SCOPE AND APPLICATION

Table 1 contains the standard compound list for this method, however, it is also applicable to other compounds, as listed in SW-846 Method 6020.

5. SUMMARY OF METHOD

This method describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be

assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

6. EQUIPMENT & SUPPLIES

- Hewlett-Packard 4500 ICP-MS equipped with a dual-channel peristaltic pump
- Neslab CFT-150 Recirculating Chiller
- Edwards Models RV8 and RV12 Vacuum Pumps
- Personal Computer with HP 4500 ChemStation Software
- High-purity Argon
- Standard Tygon 3-Stop 1.02mm-ID Peristaltic Pump Tubing (white-black)
- Standard Ismaprene 3-Stop 1.52mm-ID Peristaltic Pump Tubing (yellow-yellow)

7. REAGENTS & STANDARDS

- Type 1 Reagent Grade Water
- Ultrex II Ultrapure Hydrogen Peroxide
- Ultrex II Ultrapure Concentrated Nitric Acid
- ICP-MS Calibration Standard (CPI #4400-ICP-MSCS or other suitable vendor) containing: Al, As, Ag, Ba, Be, B, Ca, Co, Cd, Cr, Cu, Eu, Ho, La, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sc, Se, Sr, Th, Tl, U, V, Yb, & Zn @10 mg/L (from two separate sources or two different lots from the same source).
- ICP-MS Interference Check Solutions A & AB (CPI #4400-ICP-MS-ICS) or other suitable vendor).
- Tuning Solution (CPI #4400-010035 or other suitable vendor) containing Ce, Li, Tl, & Y @ 10 mg/L. Prepare a 1:1,000 dilution of this solution in 1% Ultrapure Nitric Acid for use as a 10 ug/L working tune solution.
- Internal Standard Solution (CPI #4400-010034 or other suitable vendor) containing Li^{6}, Sc^{45}, Y^{89}, In^{115}, Tb^{159}, & Bi^{209} @ 100 mg/L.
- Calibration Blank (also to be used for instrument rinse solution): 1% Ultrapure HNO_3

8. INTERFERENCES

Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very

high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been previously identified. Examples include $ArCl^+$ ions on the As^{75} signal and MoO^+ ions on the cadmium isotopes. Refer to SW-846 Method 6020 for additional information regarding the approach used to correct for molecular isobaric interferences. Correction equations for most of the common isobaric interferences are programmed into the HP 4500 Software. Additional equations can be entered as required.

Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

Memory interferences can occur when there are large concentration differences between samples or standards that are analyzed sequentially. Sample depositions on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences, which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

9. SAMPLE COLLECTION

Non-aqueous samples should be collected in glass or plastic jars (usually 4 oz.), and should be refrigerated upon receipt. Aqueous samples for total metals should be preserved to pH < 2 with HNO_3. For samples to be analyzed for dissolved metals, the samples should be filtered prior to preservation. The maximum holding time is 6 months.

10. PROCEDURE

1. Initial Start-Up/Stand-By Mode

1.1 After applying main power to the mobile laboratory, determine the voltage at which the instrument will be operating. For 240 volts, throw the high voltage snap-switch upward. For 208 volts, throw the switch downward.

1.2 Turn on the rotophase converter.

1.3 Open the front panel on the HP 4500 and turn on the main power switch, as well as the rotary pump switches.

1.4 Power up the computer system and double-click on the **ICP-MS Top** icon to load the HP ChemStation software.

1.5 From the main screen, select **Instrument Control** from the **Instrument** pull-down menu. From the resulting instrument control window, select **Vacuum On** from the **Vacuum** pull-down menu. At this point, the backing line rotary pump and the turbo pumps will switch on. The pump gages will turn green when an acceptable operating vacuum has been reached. (Allow at least 3 hours for this to occur.)

1.6 Turn on the exhaust fan. The instrument is now in **Stand-By Mode**.

2. Analysis Mode

2.1 Turn on the argon supply and set the output pressure to 90 psi.

2.2 Turn on the chiller.

2.3 Attach the sample and drain tubing assemblies to the respective peristaltic pump heads and secure the tension clamps. From the Instrument Control window, turn on the plasma by selecting **Plasma On** from the **Plasma** pull-down menu. The instrument will perform a series of sequential operations (e.g. initialize torch position, purge gases, etc.) to turn the plasma on automatically. After all meters except the interface vacuum turn green, the instrument will ignite the plasma. The instrument diagram will indicate that the plasma is on. The interface rotary pump switches on, the instrument diagram will indicate that the pump is on, and the interface vacuum meter will turn green. The title bar indicates that the instrument has changed from Standby to Analysis mode. Allow at least 30 minutes for the instrument to equilibrate before analyzing samples.

3. Tuning (to be performed daily prior to sample analysis)

3.1 Select **Tune** from the **Instrument** pull-down menu. The tune window will open.

3.2 Aspirate the 10 ppb working tune solution.

3.3 Choose **Generate Report** from the **File** pull-down menu. This will generate and print a tuning report. The following tuning parameters must comply with the minimum requirements listed below:

Mass Axis	</= 0.1 amu
Resolution	<0.9 amu @ 10% peak height
Oxide Ions	<1%
Doubly-Charged Ions	<2%
Li^{7} Sensitivity	>8,000 counts @ RSD of <15%
Y^{89} Sensitivity	>12,000 counts @ RSD of <15%
Tl^{205} Sensitivity	>12,000 counts @ RSD of <15%

3.4 For any tuning parameter that does not comply with the above requirements, complete the appropriate optimization procedure found in Section 2 of the HP 4500 Operator's Manual. (Note: Generally, optimization is not required every day, but may be needed after relocation to a job site, periods of inactivity, or system maintenance. Autotune may be used as a starting for re-tuning, but additional manual tuning may also be required.)

3.5 After obtaining a successful tune report, generate three additional tune reports. Instrument stability is verified by analyzing a tuning solution four times with an RSD of < or = 5% for the analytes contained in the solution.

3.6 Complete the tuning process by determining the P/A factors. (This is required daily.) Select **P/A Factor** from the **Tune** pull-down menu. When the P/A Factor window opens, click on the **Load Masses from Acq. Method** to load masses from the currently loaded analytical method. Aspirate a 50 ppb calibration standard and click the **Run** button. Print the resulting P/A Factor Report that opens in a separate window at the completion of the process.

4. Sample Analysis

4.1 Select **Load and Run Method** from the **Methods** pull-down menu. Choose the appropriate analytical method from the list. After the method loads, a **Load Calibration File** window will appear. Choose the appropriate calibration file from the list. (Note: The method and calibration files displayed in the pick lists can be created and/or edited by choosing **Edit Entire Method** from the **Methods** pull-down menu and following the instructions and prompts in sections 3 and 9 of the HP 4500 Operator's Manual.

4.2 Set up the analytical sequence by selecting **Edit Sample Log Table** from the **Sequence** pull-down menu. Enter the pertinent run log information (i.e.; data file name, sample name, dilutions, etc.) into the resulting spreadsheet. Refer to Section 4 of the HP 4500 Operator's Manual for additional guidance regarding the sample log table. Print the completed log table and then click **OK**.

4.3 Select **Run Sequence** from the **Sequence** pull-down menu. The Start Sequence window will open. Fill in the operator name, data batch directory, and any necessary comments. Click **Run Sequence** to start the analysis.

5. Data Analysis

5.1 Begin by choosing **Main Panel** from the **Data Analysis** pull-down menu. The data analysis main window will open.

5.2 To review the calibration information for the sample batch, select **Calibration Graph** from the **Calibrate** pull-down menu. Print the calibration information by choosing **Print Calib. Report**.

5.3 To review the mass spectrum for each sample, choose **Load** from the **File** pull-down menu. When the **Load Data File** window opens, select the data batch directory assigned to the sample group, and then select the appropriate sample data file. After review of the spectrum is complete, select **Generate Report** from the **FullQuant** pull-down menu to analyze and print the sample results.

11. CALCULATIONS

1. Water Samples

$$C(\mu g/L) = R_R \times D$$

2. Soil Samples

$$C(ug/Kg) = \frac{R_R \times V_F \times D}{W_S \times \%S}$$

Where:
C = Concentration in sample
R_R = Raw read from instrument (ppb)
D = Dilution factor of sample
%S = Percent Solid
W_S = Sample Weight (g)
V_F = Final Volume (L)

12. QUALITY CONTROL

The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the initial calibration standard (i.e.; the calibration blank), the following procedure is followed. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal standard intensities fall within the prescribed window. The intensity levels of the internal standards for the initial calibration standard (i.e., calibration blank) and the CCVs must agree within ± 20 percent. If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

Batch QC (where a batch is defined as a set of no more than 20 samples prepared at the same time with the same reagents) must comply with the following requirements:

1. Every batch must include a Method Blank (MB), a Laboratory Control Spike (LCS), a Laboratory Control Spike Duplicate (LCSD), a Post Digestion Matrix Spike (MS), and 1:5 Dilution Test Sample.

2. The MB must be less than the project specified reporting limit.

3. The results of the LCS / LCSD must be within $\pm$20% of true concentration, with the RPD $\leq$ 20% between them.

4. The MS recovery should be within ±25 % of true value. MS failures are often attributable to sample nonhomogeneity in the case of metals, increasing the importance of digesting an LCS/LCSD pair with all batches.

5. The analyte concentrations for the 1:5 Dilution Test Sample must fall within 10% of the analyte concentrations of the undiluted sample.

6. The absence of interferences must be demonstrated daily by running an ICSA and an ICSAB. The ICSA results must be less than the reporting limits for the elements of concern. The results of the ICSAB must be within 20% of true value.

13. CALIBRATION AND STANDARDIZATION

1. Prepare calibration standards at the following levels: 1, 10, 100, and 1,000 ppb. The initial calibration must be linear and have a correlation coefficient of 0.995 or better. During the course of an analytical run, the instrument may be "resloped" or recalibrated to correct for instrument drift. The correlation coefficient for the recalibration must also be 0.995 or better. A recalibration must then be followed immediately by a new analysis of a CCV and CCB before any further samples may be analyzed.

2. The calibration must be verified with a second source CCV immediately after the calibration and after every ten runs. The results must agree with the true value within 10%.

3. The CCV must be followed by a CCB. The CCB results must be less than the report limit (RL) for the elements of concern. If not, corrective action must be taken which may include instrument maintenance, rerunning samples, flagging data, etc.

14. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

Quality Control Check List

Quality Control	Frequency	Criteria
Initial Calibration	Daily	1) The regression correlation coefficient for each curve ≥ 0.995.
Initial/Continuing Calibration Check	Daily before analyses; Bracketing every ten runs.	1) The % Recovery ± 10% of true value.

Initial/Continuing Blanks	Daily before analyses; Bracketing every ten runs.	1) Blank is free of target compounds > the reporting limit.
Method Blank	One per analytical batch.	1) Blank is free of target compounds > the reporting limit.
ICSA/ICSB	Beginning and end of analytical sequence.	1) ICSA is free of target compounds > the reporting limit. 2) ICSAB % Recovery ± 20% of true value.
Matrix Spike (Post Digestion)	Once per analytical batch.	1) All project-required analytes recovered within 75-125%.
1:5 Dilution Test Sample	Once per analytical batch.	1) The % Recovery ± 10% of value in undiluted sample.
Lab Control Spike/Lab Control Spike Duplicate	Once per analytical batch.	1) All project-required analytes recovered within 80-120%. 2) % RPDs ≤ 20%
Internal Standard Intensities (in reference to calibration blank)	All samples and CCVs in batch	1) Samples: >30% & <120% 2)CCVs: +/- 20%

15. CORRECTIVE ACTION FOR OUT-OF-CONTROL DATA:

The following are appropriate corrective actions to be taken in the event of out-of-control data in the field:

1. **Tuning** – If any of the tuning parameters listed in step 3.3 above do not fall within the specified ranges, perform the optimization routines found in Section 2 of the HP 4500 Operator's Manual. If optimization routines do not remedy the problem, instrumentation maintenance activities per the Operator's Manual may be required. Notify your supervisor.

2. **Initial Calibration Verification** – If the initial calibration verification check fails, do not proceed with sample analysis. Re-run the calibration process. If the condition persists, investigate the calibration solutions for the possibility of preparation errors. Also, re-check the instrument tuning parameters and sample delivery system.

3. **Continuing Calibration Verification** – If the CCV fails, repeat the analysis once to rule out any instrument anomalies. If the condition persists, recalibrate the instrument, and then re-analyze all samples previously analyzed after the last valid CCV.

4. **Initial and Continuing Calibration Blanks** – Failures here are usually indicative of cross-contamination, particularly after analysis of high concentration samples. Clean out the sample delivery system. Consider changing out the sample pump tubing and/or increasing the rinse time.

5. **ICSA & ICSAB** – If analysis of these samples fails, suspect problems with the interference correction equations and/or the isotopes chosen for quantification. Do not proceed with analysis of affected analytes until the problem has been corrected. Refer to section 3 of the HP 4500 Operator's Manual.

6. **Internal Standard Intensity** – If inconsistencies in the IS intensities occur among the calibration blank and the CCVs, terminate the analysis, re-tune the instrument, recalibrate, verify the new calibration, and reanalyze the affected samples.

7. **Hold Time** – Any sample analysis beyond the given hold time needs to be qualified, and have it clearly stated in the comment section of the report.

8. **Results Beyond the Linear Range** – Samples that attain results beyond the highest calibration standard need to be rerun at an appropriate dilution. Each analyte should be reported from the analysis with the smallest dilution in which the result is in the linear range. Any result reported from a secondary dilution should use the "D" qualifier in the QC line of the report. Furthermore, analyses directly after grossly contaminated samples need to be monitored for possible carryover. Any analyte that has results beyond the highest point in the curve will be considered possible contamination in the following sample. All samples affected will be marked with the appropriate qualifier, and will be reanalyzed. Both results should be reported.

16. SAFETY

Safety glasses are required at all times in all laboratories. Due to the use of strong acids in this method, protective gloves and lab coats are recommended in the laboratory. On all projects, chemists need to be aware of, and adhere to the New Age/Landmark Health and Safety Plan, and any site-specific health and safety requirements

17. POLLUTION PREVENTION AND WASTE MANAGEMENT

All samples received and analyzed on-site will be returned to the client's representative for proper disposal. New Age staff is not authorized to take permanent possession or dispose of any samples. **Unless authorized by the client and the President, samples are not to be removed from the project site.** Unless specific stipulations are made to dispose of lab waste on the project site, digestates are brought back to the fixed lab and disposed of in the appropriate acid waste barrel.

18. REFERENCES

United States Environmental Protection Agency, "Method 6020, Test Methods for Evaluating Solid

Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 0, September 1994.

United States Environmental Protection Agency, "Method 3050B, Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 0, December 1996.

United States Environmental Protection Agency, "Method 3010B, Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 0, December 1996.

USACE Interim Chemical Data Quality Management Policy for Hazardous, Toxic, and Radioactive Waste Projects.

19. TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

TABLE 1
Method Detection Limits and Reporting Limits (PPB)

Element	IDL	RL	Element	IDL	RL
Ag	0.009	1.0	**Mn**	0.024	1.0
As	0.010	1.0	**Mo**	0.008	1.0
Ba	0.086	1.0	**Ni**	0.081	1.0
Be	0.098	1.0	**Pb**	0.012	1.0
Cd	0.010	1.0	**Sb**	0.007	1.0
Co	0.050	1.0	**Se**	0.027	1.0
Cr	0.031	1.0	**Tl**	0.007	1.0
Cu	0.014	1.0	**Zn**	0.029	1.0
Li	0.084	1.0			

New Age/Landmark
Mobile Laboratory Services
667 West Main Street
Benton Harbor, MI 49002
Phone (616) 927-3004 Fax (616) 927-3411

Analysis Date:	**5/5/06**	**5/5/06**	**5/5/06**	**5/5/06**	**5/5/06**	**5/5/06**	**5/5/06**			
Operator:	SDW	SDW	SDW	SDW	SDW	SDW	SDW			
Matrix:	Soil	Soil	Soil	Soil	Soil	Soil	Soil			
Method:	6020	6020	6020	6020	6020	6020	6020			

ANALYTES		MDL#1 (ug/Kg)	MDL#2 (ug/Kg)	MDL#3 (ug/Kg)	MDL#4 (ug/Kg)	MDL#5 (ug/Kg)	MDL#6 (ug/Kg)	MDL#7 (ug/Kg)	Mean	Standard Dev.	MDL
Lithium	Li-7	78.56	70.57	55.29	95.62	74.07	90.53	68.45	75.084	13.672	**41.02**
Beryllium	Be-9	72.65	76.39	71.78	69.87	74.02	73.16	71.57	72.752	2.068	**6.20**
Vanadium	V-51	135.4	109.7	87.64	135.7	131.7	129	109.7	118.557	18.077	**54.23**
Chromium	Cr-53	94.37	100.2	90.26	99.51	104.4	98.25	93.7	97.142	4.756	**14.27**
Manganese	Mn-55	35.45	34.36	34.69	39.18	35.8	35.82	34.43	35.644	1.664	**4.99**
Cobolt	Co-59	82.53	80.53	80.6	81.94	81.98	81.79	80.7	81.435	0.810	**2.43**
Nickel	Ni-61	72.11	129.6	123.1	148.7	166.5	183.1	151	134.287	35.950	**107.85**
Copper	Cu-63	42.8	41.29	42.69	43.26	40.94	40.87	41.44	41.889	0.987	**2.96**
Zinc	Zn-66	90.62	88.68	86.34	81.75	86.03	88.9	90.27	87.465	3.091	**9.27**
Arsenic	As-75	75.12	74.61	74.5	70.93	71.75	70.78	69.83	72.475	2.177	**6.53**
Selenium	Se-82	85.66	86.67	85.49	81.22	83.99	80.15	82.37	83.619	2.465	**7.39**
Molybdenum	Mo-98	78.48	76.11	76.87	77.69	76.41	75.34	76.04	76.699	1.072	**3.22**
Silver	Ag-109	102.1	102.1	102.1	101	100.9	102	101	101.599	0.594	**1.78**
Cadmium	Cd-111	77.49	78.08	80.02	79.72	79.5	81.01	83.08	79.825	1.855	**5.57**
Tin	Sb-123	73.53	74.03	76.18	74.24	74.64	73.31	75.45	74.477	1.032	**3.10**
Barium	Ba-137	32.18	29.69	34.12	32.28	31.97	30.62	34.09	32.100	1.637	**4.91**
Thallium	Tl-205	80.51	79.5	77.7	79.24	79.18	79.64	80.09	79.404	0.889	**2.67**
Lead	Pb-208	37.26	37.04	38.4	39.1	37.4	37.94	37.6	37.814	0.723	**2.17**

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667 West Main Street
Benton Harbor, MI 49002
Phone (616) 927-3004 Fax (616) 927-3411

		Method:	6020	6020	6020	6020	6020	6020	6020			
ANALYTES	**ANALYTES**	**True Value (ug/L)**	**MDL#1 (ug/L)**	**MDL#2 (ug/L)**	**MDL#3 (ug/L)**	**MDL#4 (ug/L)**	**MDL#5 (ug/L)**	**MDL#6 (ug/L)**	**MDL#7 (ug/L)**	Mean	Standard Dev.	**MDL**
Lithium	**Li-7**	0.5	0.5451	0.4999	0.5602	0.3701	0.4629	0.4552	0.5085	0.482	0.064	0.19
Beryllium	**Be-9**	0.5	0.5243	0.5008	0.5116	0.5074	0.4674	0.5017	0.4809	0.499	0.019	0.06
Vanadium	**V-51**	0.5	1.9720	2.2500	2.0980	1.9130	2.1530	2.1260	2.2650	2.107	0.131	0.39
Chromium	**Cr-53**	0.5	1.0080	1.0570	0.9924	0.9568	1.1080	1.0400	1.1190	1.039	0.060	0.18
Manganese	**Mn-55**	0.5	0.1604	0.1366	0.1384	0.1136	0.1456	0.1415	0.1384	0.139	0.014	0.04
Cobolt	**Co-59**	0.5	0.5288	0.5342	0.5277	0.5100	0.5399	0.5163	0.5411	0.528	0.012	0.03
Nickel	**Ni-60**	0.5	0.3109	0.3103	0.3006	0.2987	0.3256	0.3013	0.3247	0.310	0.011	0.03
Copper	**Cu-65**	0.5	0.1786	0.1768	0.1595	0.1583	0.1673	0.1610	0.1781	0.168	0.009	0.03
Zinc	**Zn-68**	0.5	0.1596	0.1229	0.1958	0.2002	0.1559	0.2002	0.1519	0.167	0.030	0.09
Arsenic	**As-75**	0.5	0.3999	0.3662	0.3906	0.3890	0.4055	0.3903	0.4084	0.393	0.014	0.04
Selenium	**Se-82**	0.5	0.5460	0.4999	0.5324	0.5746	0.5511	0.5473	0.5430	0.542	0.023	0.07
Molybdenum	**Mo-95**	0.5	0.4875	0.4699	0.4806	0.4607	0.4627	0.4817	0.4547	0.471	0.012	0.04
Silver	**Ag-109**	0.5	0.7369	0.7062	0.7143	0.6973	0.7116	0.7113	0.7252	0.715	0.013	0.04
Cadmium	**Cd-111**	0.5	0.5306	0.5062	0.5300	0.4875	0.4806	0.4901	0.5292	0.507	0.022	0.07
Tin	**Sb-123**	0.5	0.5041	0.4702	0.5049	0.4771	0.4907	0.4850	0.5014	0.490	0.014	0.04
Barium	**Ba-135**	0.5	0.0432	0.0167	0.0703	0.0396	0.0201	0.0221	0.0599	0.034	0.021	0.06
Thallium	**Tl-205**	0.5	0.4970	0.5241	0.5200	0.5355	0.5133	0.5099	0.5203	0.517	0.012	0.04
Lead	**Pb-208**	0.5	0.2223	0.2566	0.2588	0.2567	0.2495	0.2510	0.2764	0.253	0.016	0.05

FIELD PROCEDURE HGAA-001 MERCURY

ANALYSIS OF MERCURY IN SOLIDS AND SOLUTIONS BY THERMAL DECOMPOSITION, AMALGAMATION, AND ATOMIC ABSORPTION SPECTROPHOTOMETRY by EPA Method SW-846 7473

SCOPE AND APPLICATION:

Total mercury (organic and inorganic) in soils, sludges, aqueous wastes, groundwaters, leachates, and fish tissues may be determined by this method without chemical pretreatment. This method may also be applied to the detection of total mercury in digests obtained from SW-846 3000 series methods.

SUMMARY OF METHOD:

Controlled heating in an oxygenated decomposition furnace is used to liberate mercury from solid and aqueous samples in the instrument. The sample is dried and then thermally and chemically decomposed within the decomposition furnace. The decomposition products are carried by flowing oxygen to the catalytic section of the furnace. Here oxidation is completed and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to an amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamator is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance is measured at 253.7 nm as a function of mercury concentration.

The working range for this method is 0.05 – 600 ng. The mercury vapor is first carried through a long and then a short path length absorbance cell. (The length of the first cell and the second cell are in a ratio of 10:1.) The same quantity of mercury is measured twice, using two different sensitivities, resulting in a dynamic range that spans at least four orders of magnitude. Method Detection Limits (MDLs) are determined annually for all matrices tested and copies thereof are kept both with the instrument and at the main office.

DEFINITIONS:

1. Thermal Decomposition: Partial or complete degradation of sample components using convection and conduction heating mechanisms resulting in the release of volatile components such as water, CO_2, organic substances, elements in the form of oxides or complex compounds, and elemental gases.

2. Amalgamation: The process by which mercury forms a metal alloy with gold.
3. Amalgamator: A system composed of gold particles at a high surface area to volume ratio for the purpose of amalgamating mercury vapor.
4. Sample Boat: The non-amalgamating thermally stable vessel used for containment and transport of the solid or liquid sample for thermal decomposition.

INTERFERENCES:

1. Carryover may be a problem after running samples with concentrations of 400ng or higher.
2. Co-absorbing gases, such as free chlorine and certain organics.

SAFETY:

1. Refer to SW-846 Chapter Three for a discussion on safety related references and issues.
2. Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of concentrated mercury reagents. Concentrated mercury reagents should only be handled by analysts knowledgeable of their risks and of safe handling procedures.

EQUIPMENT:

- Milestone mercury analyzer model DMA-80 with autosampler
- Toshiba laptop computer with DMA-80 Rev. 4.0.0.76 software
- Metal sample boats with 0.5 mL capacity
- Eppendorf adjustable pipettor (10-100 μL)
- VWR adjustable pipettor (100 – 1000 μL)
- Oxygen gas

REAGENTS:

- Purchased 1000-ppm mercury standard (primary and secondary source).
- Concentrated Nitric Acid
- Reagent water

SAMPLE COLLECTION, PRESERVATION, AND HANDLING:

Samples should be collected in acid-rinsed plastic, glass, or PTFE containers. The maximum holding time is 28 days. Aqueous samples should be preserved with HNO_3 to pH < 2. If solid samples are not analyzed immediately, refrigeration to 4^{o}C is necessary.

PREPARATION OF STANDARDS:

1) Prepare a 1-ppm working standard by adding 0.100 mL 1000 ppm Hg Standard to a 100-mL volumetric flask containing 10-mL nitric acid and diluting to volume with reagent H_2O.
2) Transfer standard to a glass amber bottle and store away from light. Maximum hold time is one month.
3) Prepare the calibration check standard in the same manner as described in steps 1 and 2 above from a second source 1000-ppm stock standard.

CALIBRATION AND STANDARDIZATION:

1) Primary calibration: The instrument is calibrated in two different working ranges: the low range is 0-40 ppb Hg and the high range is 40-600 ppb Hg. Calibrate the instrument following the instructions for "Calibration Process using Aqueous Hg Standard" in the **Getting Started-Calibration and Analysis Procedure** Manual for the DMA-80. Both curves must have at least 5 points. The software will not provide a correlation coefficient, so enter the concentration and absorption information for both curves into the excel spreadsheet named Calibration Curve to verify they are 0.995 or better, print out the spreadsheet, and file it with the curve.
2) Daily calibration: The high and low concentration standards (0.025 and 0.250 ppm) are analyzed using the analytical parameters that are to be employed for the type of samples to be analyzed. The results must be within 10% of their true value for the curve to be considered valid. (Before recalibrating, try making fresh standards as Hg standards are photosensitive and degrade easily when exposed to light.). These Continuing Calibration Verifications (CCVs) must be followed by instrument or method blanks.

PROCEDURE:

1) General analytical parameters: the analytical parameters depend on the sample size and matrix. Use the following table to determine which to use:

Sample Type	Maximum Capacity	Drying time (s)	Decomposition Time (s)	Wait Time (s)
Aqueous	500 µL	Sample volume (µL) x 0.7 sec. @ 300°C	150 sec.	45
Fish Tissue	400 mg	70 sec. @ 300°C	180 sec.	60
Solid	500 mg	90 sec. @ 300°C	240 sec. *	60

* For samples with high organic content, observe the energy bar after the first read. If it is not back up to 98% by the time the next read starts, increase the decomposition time

by increments of 30 seconds.

General methods for these three matrices are stored in the software.

2) Turn on the oxygen at the tank. The regulator should be set to 60 PSI.
3) Turn on the instrument and boot up the Toshiba laptop.
4) Start the software by clicking on the DMA-80 icon; making sure the authorization card is in the chip card reader.
5) Allow the instrument to warm up for approximately one half hour. When all heated zones are at the proper temperature, the four bar charts under "Heating Control" on the System page will be green and read "OK."
6) Set up a new file daily on the Editor page by first selecting the appropriate method. Then click on the "+" symbol under the Data side of the screen and type in the date in the Name field. Make sure to type in SW-846 7473 under the Description field. Select either Auto sampling mode for solids and fish tissue or Single for aqueous samples.
7) Go to the Calibration page and ensure the latest calibration is selected by clicking next to it. (When starting the software the last calibration used automatically becomes active again.)
8) Set up the ID-weight file by going to the Documentation screen. The file name and date will automatically be filled in. Make sure to enter the your initials under the Operator field.
9) Solid (fish tissue or soil) Sample analysis:
   a) Begin the sequence with both a low-level and high-level CCV, followed by a blank.
   b) Homogenize the sample by stirring thoroughly in the case of soils, or cut a piece of filet in the case of fish tissue and weigh 500 mg to the nearest 0.001 of a gram onto a tared sample boat. Insert boat into the instrument.
   c) Enter the identification and weight for each sample on the Documentation page. Unless a weight is entered the sample will not run.
   d) If a dilution is necessary, weight a lesser portion of the sample.
   e) Begin analysis by pressing "Start" on the System page.

10) Aqueous samples (including digests or extracts):
   a) Begin the sequence with both a low-level and high-level CCV, followed by a blank.
   b) Homogenize the sample by shaking well and pipet 500 μL. For TCLP extracts a single run with no concentration is sufficient with a reporting limit of 1 ppb. For aqueous samples a six-fold concentration is necessary to reach a detection limit of 0.2 ppb. This is accomplished as follows:
      i) Introduce sample into the boat.
      ii) Select a new line in the Documentation table by clicking on the "+" symbol at the bottom of the screen, and click on the "Concentrate" button in the upper right hand part of the screen. Enter the sample ID and volume in the weight column as usual and press "Start" on the System page.
      iii) Repeat Step (ii) five more times. For the last (sixth) sample, click on the "End-Concentrate" button. This will automatically release all of the mercury collected

from the six aliquots and calculate the result using the sum of the volumes/weights used.

DATA ANALYSIS AND CALCULATIONS:

Calculate metal concentrations: (1) by the method of standard addition, or (2) directly from the instrument's concentration read-out. The direct read for soils must be corrected by dividing by the percent solids or it must be noted on the report that the result is reported on a wet-weight basis. It is customary to report fish tissue on a wet-weight basis.

QUALITY CONTROL:

1) Run QC:
   a) Perform daily calibration as described in part two of the Calibration and Standardization Section.
   b) The working standard curves must be verified by analyzing a 0.025-ppm and a 0.250-ppm standard at the beginning and end of every analytical batch. This standard value must be within 15% of the true value, or the previous samples must be reanalyzed.

2) Batch QC (where a batch is defined as a set of no more than 20 samples prepared at the same time with the same reagents):
   a) Every batch must include a Method Blank (MB), a Laboratory Control Spike (LCS), a Matrix Spike (MS), and a Matrix Spike Duplicate (MSD). The spikes should be either at the project-specified action level or between the low and midlevel standards.
   b) The MB must be less than the project specified reporting limit.
   c) The results of the LCS must be within $\pm$15 % of true concentration
   d) The MS/MSD recoveries must be within $\pm$15 % of true value, and $\leq$20 relative percent difference.
   e) Dilution Test: For each analytical batch select one typical sample for serial dilution to determine whether interferences are present. The concentration of the analyte should be at least 25 times the estimated detection limit. Determine the apparent concentration in the undiluted sample. Dilute the sample by fivefold and reanalyze. The diluted and undiluted results must agree within 10%, or method of standard additions must be used. If all samples in the batch are below 10 times the detection limit, use the spike recovery analysis described below.
   f) Recovery Test: If results from the dilution test do not agree, a matrix interference may be suspected and a spiked sample should be analyzed to help confirm the finding from the dilution test. Withdraw another aliquot of the test sample and add a known amount of analyte to bring the concentration of the analyte to 2 to 5 times the original concentration. If all of the samples in the batch have analyte concentrations below the detection limit, spike the selected sample at 20 times the detection limit. Analyze the spiked sample and calculate

the spike recovery. If the recover is less than 85% or greater than 115%, the method of standard additions shall be used for all samples in the batch.

METHOD PERFORMANCE:

Refer to Method SW-846 7473 Section 13.0 for method performance information.

POLLUTION PREVENTION:

In addition to following good laboratory procedures and all of those promulgated in New Age's Quality Assurance Manual, refer to section 14.0 of SW-846 7473 for information concerning pollution prevention.

WASTE MANAGEMENT:

Refer to New Age's Quality Assurance Manual, Section 3.3.5.

REFERENCES:

1. Milestone, Inc., DMA-80 Operating Manual, 160B Shelton Rd., Monroe, CN 06468
2. Milestone, Inc., Getting Started: Calibration and Analysis Procedure, 160B Shelton Rd., Monroe, CN 06468
3. EPA SW-846 Chapter Three
4. EPA SW-846 Method 7000 Section 8.7 (for in-depth discussions of Method of Standard Additions)
5. EPA SW-846 Method 7473
6. New Age / Landmark, Inc. Quality Assurance Manual, Rev. 7

EPA 7473 Quality Control Check List

Quality Control	Frequency	Criteria
Initial Calibration (at least five pts of project specific compounds).	As required	1) The regression correlation coefficient for each curve $\geq$ 0.995. 2) Low level check standard $\pm$20%
Initial/Continuing Calibration Check	Daily before analyses; Bracketing every ten runs.	1) The ICV % Recovery $\pm$ 10% of true value. 2) The CCV % Recovery $\pm$ 20% of true value.
Initial/Continuing Blanks	Daily before analyses; Bracketing every ten runs.	1) Blank is free of target compounds > the reporting limit.
Method Blank	One per analytical batch.	1) Blank is free of target compounds > the reporting limit.
ICSA/ICSB	Beginning and end of analytical sequence.	1) The % Recovery $\pm$ 20% of true value.
Matrix Spike/Matrix Spike Duplicate	Once per analytical batch.	1) All project-required analytes recovered within 80-120%.
		2) % RPDs $\leq$ 25%
Lab Control Spike/Lab Control Spike Duplicate (if required)	Once per analytical batch.	1) All project-required analytes recovered within 80-120%.
		2) % RPDs $\leq$ 25%